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Control of Air Pollution Emissions from Molybdenum Roasting. Volume 3. Pilot Scale Test Results for Magnesium Oxide Scrubbing

Molycorp, Inc., Washington, PA

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CONTROL OF AIR POLLUTION EMISSIONS FROM MOLYBDENUM ROASTING
VOLUME III

PILOT SCALE TEST RESULTS FOR MAGNESIUM OXIDE SCRUBBING

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16. ABSTRACT

A research project was conducted to determine the feasibility of applying the magnesium oxide (MgO) scrubbing system to smelter off-gas streams containing approximately one percent SO_2. Pilot scale (4000 Nm^3/hr) tests of the MgO system using a packed tower absorber with no regeneration of the MgO solids were conducted at Molycorp, Inc.'s molybdenum roaster. During the test program, process parameters were varied to observe their effect on SO_2 removal, and data collected were correlated in a design equation. Test results indicated that the MgO scrubbing system was capable of removing over 90 percent of the SO_2 from an off-gas stream containing up to 9000 ppm SO_2. The outlet SO_2 concentration of the packed bed should be maintained above 500 ppm to prevent plugging of the bed with $MgSO_3$ solids. The design equation developed to correlate the test results gave excellent correlation with the experimental data. Certain issues were not addressed during the test program because the pilot unit was not operated as a closed-loop system. Of these, it appears that the buildup of $MgSO_4$ (aq) would have the largest impact on the test results.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This document is one of a series of three reports resulting from a program to define the emissions control problems and explore applicable systems to control emissions from a molybdenum roaster. The program was jointly sponsored by Molycorp, Inc. and the Industrial Environmental Research Laboratory - Cincinnati to: (1) determine the capabilities of a unique fabric filtration system using teflon coated bags in a hot, corrosive atmosphere for particulate and trace element control and (2) to explore the feasibility of a variety of weak SO_2 control systems for application to the moly roaster and potentially to other smelter weak SO_2 off-gases.

David G. Stephan
Director
Industrial Environmental Research Laboratory
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ABSTRACT

A research project was conducted to determine the feasibility of applying the magnesium oxide (MgO) scrubbing system to smelter off-gas streams containing approximately one percent SO_2. The objectives of the project were to quantify the SO_2 removal which could be obtained by the MgO system and to develop design data on the MgO system which could be used to design an absorber for treating similar gas streams. To meet these objectives, pilot scale ($\sim$4000 Nm^3/hr) tests of the MgO system using a packed tower absorber with no regeneration of the MgO solids were conducted at Molycorp, Inc.'s molybdenum roaster. During the test program, process parameters were varied to observe their effect on SO_2 removal, and data collected were correlated in a design equation.

Test results indicated that the MgO scrubbing system was capable of removing over 90 percent of the SO_2 from an off-gas stream containing up to 9000 ppm SO_2. The outlet SO_2 concentration of the packed bed should be maintained above 500 ppm to prevent plugging of the bed with $MgSO_3$ solids. The design equation developed to correlate the test results gave excellent correlation with the experimental data. Certain issues were not addressed during the test program because the pilot unit was not operated as a closed-loop system. Of these, it appears that the buildup of $MgSO_4$ (aq) would have the largest impact on the test results.

Comparison of the pilot plant test results to these reported for utility applications of the MgO system indicate that the pilot plant was generally superior. The packed absorber appears well suited to treating off-gas streams which contain high concentrations of SO_2 (up to 9000 ppm). If the MgO system is considered for application to an SO_2 stream containing $\sim$1 percent SO_2, it is recommended that further test work should be conducted on a larger scale. Also, this test work should be conducted on a closed-loop system to verify the expected impact of $MgSO_4$ (aq) buildup and to demonstrate the operation of the entire MgO process.

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SECTION 1

SUMMARY

This report is an account of a research project to generate engineering design data for magnesium oxide scrubbing of a weak sulfur dioxide off-gas from a smelter. The research project consisted of pilot-scale (4000 Nm^3/hr) tests of a magnesium oxide (MgO) SO_2 scrubbing system processing off-gas from a molybdenum roaster. The test program was conducted at Molycorp Inc.'s Washington, Pennsylvania molybdenum roaster during the period of June through September 1979.

1.1 OBJECTIVES AND APPROACH

The overall goal of the test program was to determine the feasibility of applying the MgO scrubbing system to an off-gas stream having an SO_2 concentration of approximately one percent. More specifically, the objectives of the test program were:

- to quantify the SO_2 removal which could be attained by the MgO system, and
- to develop data on the MgO system which could be used to design an absorber for treating similar gas streams.

The approach used to meet the program objectives involved pilot-scale ($\sim$4000 Nm^3/hr) testing of the MgO system. A well defined test program was developed in which the process parameters of interest were varied to observe their effect on SO_2 removal. The data collected during these tests were then correlated in the form of a design equation. No regeneration of MgO was

attempted with the produced scrubber solids. Additionally, obtaining long-term process reliability and operability data about the process was not an objective.

Pilot Plant Description

The pilot plant which was used to test the MgO system consisted of an absorber, a reaction tank, a clarifier and overflow tank, and a reagent feed tank. The absorber was a 76 cm (30 inch) diameter tower containing two beds of 2.5 cm (1 inch) tellerette packing. The upper bed depth was 76 cm (30 inches) and the lower bed was 51 cm (20 inches) deep. The piping and valve arrangement was designed to distribute slurry through both beds or the lower bed only. This permitted scrubbing tests at packing depths of 51 cm (20 inches) and 127 cm (50 inches). Full cone spray nozzles were used for liquid distribution and were arranged so that the outer edge of the cone contacted the tower wall at the level of the packing.

Gas flow rates through the absorber ranged from 2800 to 4000 Nm^3/hr (1700 to 2600 scfm) while slurry flow rates ranged from 0.4 to 2.4 ℓ/sec (6 to 38 gpm). During most tests, the pH of the absorber feed was maintained between 7.5 and 8.0. Slurry exiting the absorber was gravity-fed to a 5700 ℓ (1500 gallon) reaction tank. The pH of the slurry leaving the absorber ranged from 4.5 to 6.5. $Mg(OH)_2$ slurry was added to the reaction tank to maintain the pH at 7.5-8.0.

Test Plan

The first step in evaluating the performance of the MgO system involved development of a test plan which systematically examined the effect of varying important absorber operating parameters. The operating parameters of principal interest include:

- liquid-to-gas ratio in the absorber,
- gas flow rate in the absorber, and
- packing depth in the absorber.

The test plan developed to examine these parameters consisted of a matrix of short-term tests which included all possible combinations of three liquid-to-gas ratios, three gas flow rates, and two packing depths (18 tests). These tests were supplemented with a limited number of tests in which the pH of the scrubbing slurry and the SO_2 concentration of the off-gas were varied. In addition, a longer-term, or steady-state test was scheduled. This test was included to provide data which would be used to complete material balance calculations for the system.

1.2 TEST RESULTS

The tests conducted at Molycorp's plant indicated that the MgO scrubbing system is applicable for treating gas streams containing up to about one percent SO_2. Removal efficiencies of over 90 percent were possible at gas velocities and absorber pressure drops similar to those used in design of utility MgO FGD systems.

Design Equation Development

In evaluating the results of the tests conducted at Molycorp, a correlation was developed which can be used to predict SO_2 removal in the pilot plant for a given set of absorber operating parameters. This correlation was developed based on absorption theory. Using the model for the two-film theory of mass transfer, it can be shown that Equation 1-1 describes the molar flux of component A (N_A) from the gas to the liquid phase.

$$N_A = K_g P (Y_A - Y_A^*) \text{ (mole/cm}^2\text{-sec)} \qquad (1\text{-}1)$$

where K_g = overall gas phase mass transfer coefficient
P = pressure in the absorber
Y_A = bulk gas phase mole fraction of component A
Y_A^* = equilibrium mole fraction of component A in the gas phase

Integrating this equation over a differential element of scrubber volume and assuming $Y_A^* << Y_A$, the removal (R) of component A in the absorber can be expressed by Equation 1-2 (see Appendix C for derivation).

$$R = 1 - \exp(-K_g a P D A_c / G) \qquad (1\text{-}2)$$

where a = interfacial area for mass transfer

D = packing depth

A_c = cross section area of the absorber

G = molar gas flow rate in the absorber

Using this form of the expression for removal, it is possible to develop an empirical expression for the product $K_g a$ as a function of the absorber operating parameters examined during the test program.

Because it is difficult to quantitatively describe $K_g a$ based on theoretical considerations, especially in a system where chemical reaction takes place, it was necessary to arbitrarily select a form of the equation for $K_g a$. The form chosen is presented in Equation 1-3.

$$K_g a = b_0 \cdot \left(\frac{L}{A_c}\right)^{b_1} \cdot \left(\frac{G}{A_c}\right)^{b_2} \cdot \left(pH\right)^{b_3} \cdot \left(W\right)^{b_4} \cdot \left(SO_2\right)^{b_5} \qquad (1\text{-}3)$$

where $\frac{L}{A_c}$ = slurry velocity in the absorber (ℓ/sec $\cdot$ m^2)

$\frac{G}{A_c}$ = gas velocity in the absorber (Nm^3/hr $\cdot$ m^2)

pH = pH of absorber feed slurry

W = weight percent $MgSO_3$ solids in the absorber feed

SO_2 = SO_2 concentration of inlet gas (ppm)

and b_0 through b_5 are empirical constants which must be determined based on experimental data.

Using statistical analysis of the experimental data from the short-term variable tests, the constants b_0 through b_5 were determined to have the following values:

$$b_0 = 4.36 \cdot 10^{-3}$$
$$b_1 = 0.899$$
$$b_2 = 1.00$$
$$b_3 = 2.86$$
$$b_4 = 0.284$$
$$b_5 = -0.621$$

Including these values in Equation 1-3 and substituting the $K_g a$ in Equation 1-2, SO_2 removal as a function of absorber operating parameters is quantified by Equation 1-4.

$$R = 1 - \exp\left[(-4.36 \cdot 10^{-3}) \left(\frac{L}{A_c}\right)^{0.899} (pH)^{2.86} (W)^{0.284} (SO_2)^{-0.621} (P)(D)\right] \quad (1\text{-}4)$$

The units for use in Equation 1-4 are as follows: L-ℓ/sec, SO_2-ppm, P-atm, D-cm, A_c-m^2. It is interesting to note that in Equation 1-4, the flue gas flow rate does not appear. This is due to an offsetting effect associated with a change in gas flow rate into the absorber. By increasing gas rate, more SO_2 enters the absorber and thus tends to lower removal. However, increasing the gas flow rate increases the value of $K_g a$ (Equation 1-3) and thus offsets the effect of additional SO_2 entering the absorber. The reader is cautioned that this is only true because the exponent of $(\frac{G}{A_c})$ is 1.0 for the test program data when using Equation 1-3.

Figure 1-1 illustrates the ability of Equation 1-4 to predict SO_2 removal as a function of absorber operating parameters. As shown, the correlation between actual and predicted removal is quite good with a correlation coefficient of 0.98.

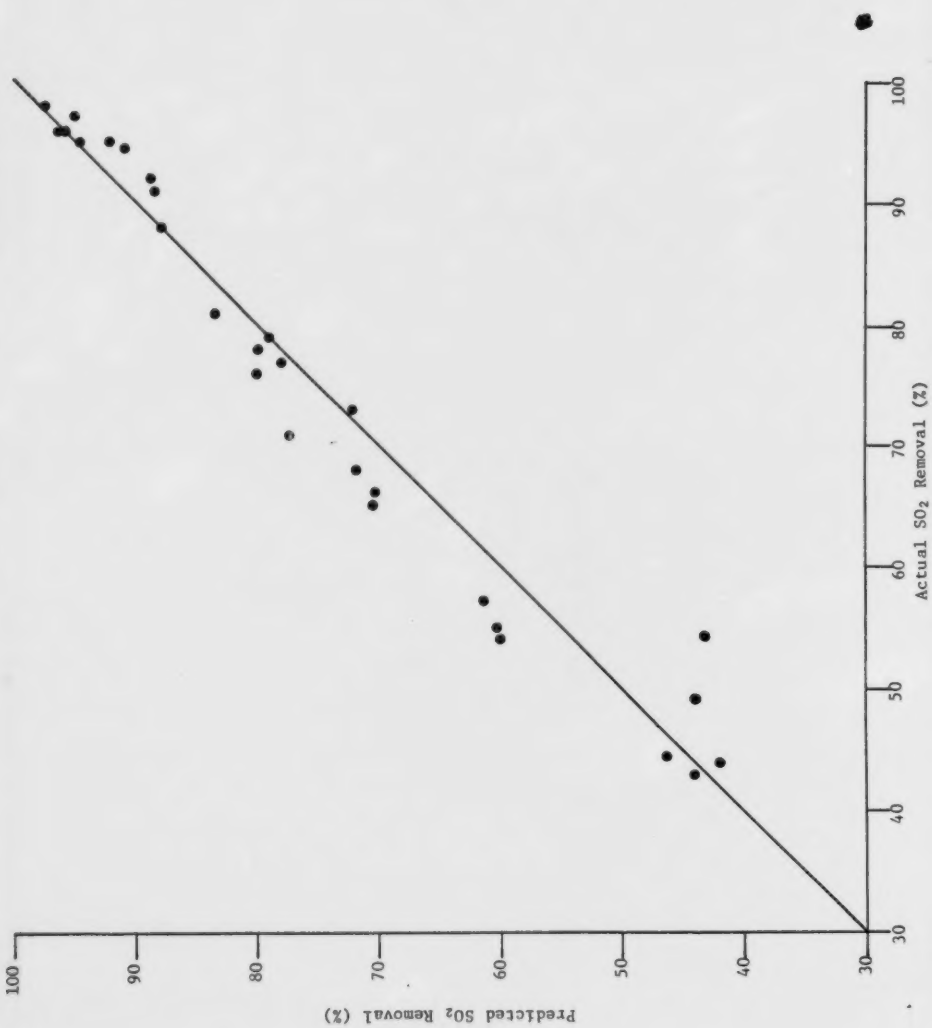

Figure 1-1. Ability of design equation to predict SO_2 removal efficiency.

Figures 1-2, 1-3 and 1-4 give a further indication of how well Equation 1-4 predicts actual test results. These figures show predicted removal as a function of L/G, pH, and SO_2 concentration respectively. In addition, actual test data points are shown in the figures. The data points presented represent tests conducted to quantify the relationship between SO_2 removal efficiency and the scrubber operating parameters. As shown, Equation 1-4 closely approximates the actual behavior observed during the test program.

Design Equation Applicability

Equation 1-4 represents an absorber design equation which can be used to predict the performance of a particular absorber design configuration. However, this equation is only valid for specific conditions and ranges of absorber operating parameters. The following discussion identifies the major restrictions which must be observed in applying Equation 1-4 to a particular situation.

The most obvious restriction on Equation 1-4 is that it is only applicable for use with an MgO scrubbing system processing gas in an absorber packed with 2.5 cm (1 inch) tellerette packing. This design equation is not applicable to other absorber configurations (*e.g.*, a spray tower) or other types of packing material. The other principal restriction on the use of Equation 1-4 is that the scrubber operating parameters selected for an absorber design must be within the range in which the parameters were tested during the program. Specific ranges for these parameters are presented in Table 1-1. The applicable range for each parameter represents the range over which the parameters were varied during the test program. However, in some cases, there are design considerations which limit the ranges presented in Table 1-1. For example, process equipment restrictions might limit the weight percent solids, and the trade-off between absorber cross-section and pressure drop affects the selection of gas velocity.

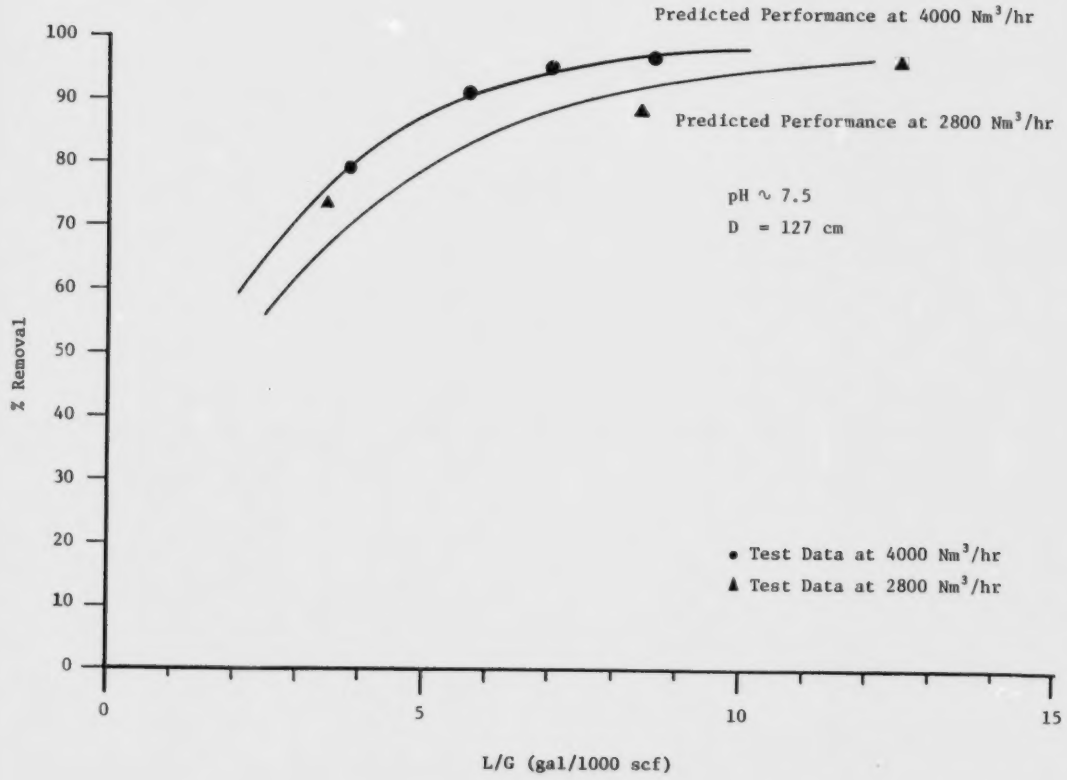

Figure 1-2. Agreement of predicted and selected experimental values for SO_2 removal as a function of L/G ratio.

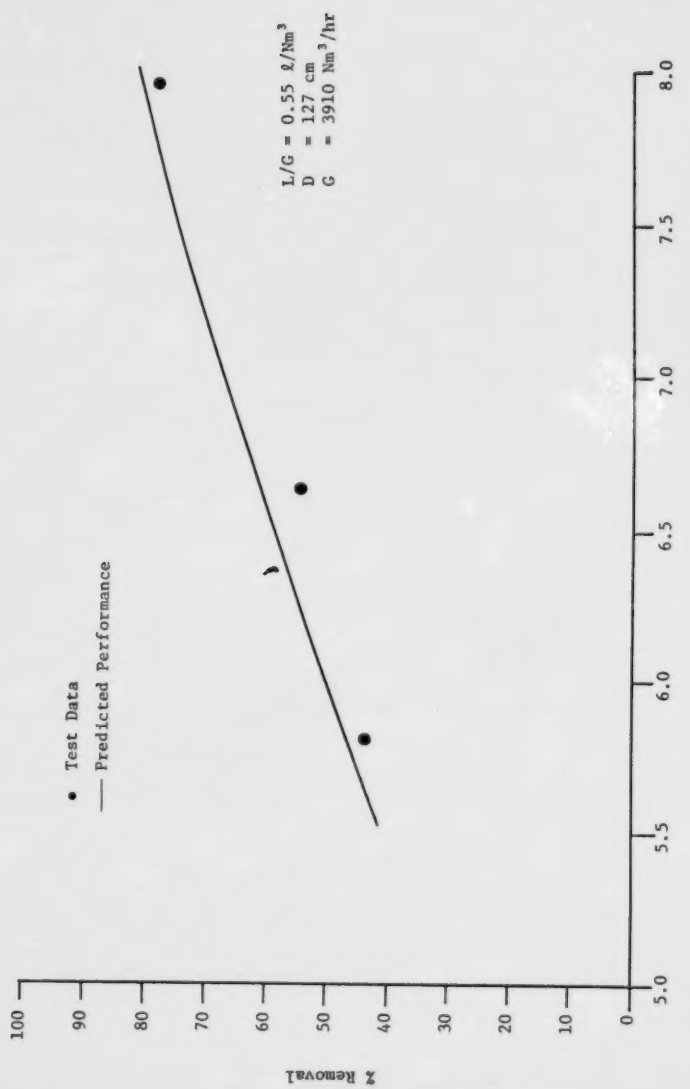

Figure 1-3. Agreement of predicted and selected experimental values for SO_2 removal as a function of absorber feed pH.

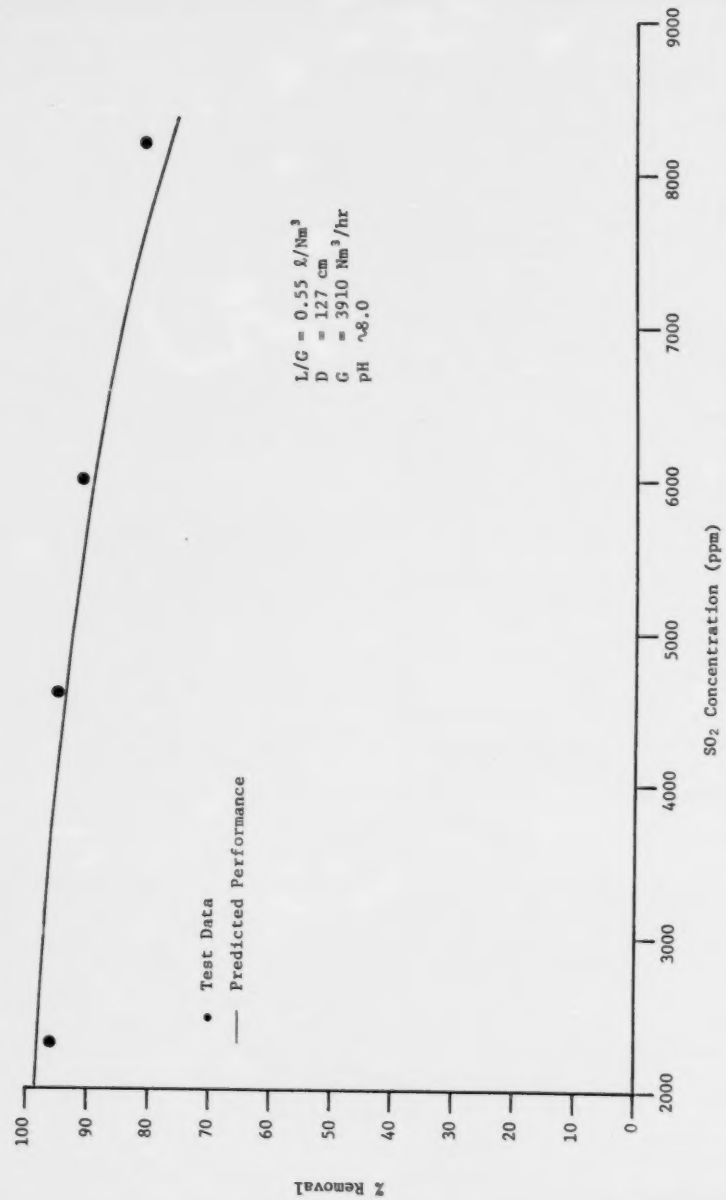

Figure 1-4. Agreement of predicted and selected experimental values for SO_2 removal as a function of inlet SO_2 concentration.

TABLE 1-1. RANGE OF ABSORBER OPERATING PARAMETERS APPLICABLE TO DESIGN EQUATION

Operating parameter	Applicable range
Gas Velocity (m/sec)	1.8 to 2.6
pH	6.0 to 8.0
Liquid Velocity (ℓ/sec·m^2)	1.0 to 5.4
Weight Percent Solids	4 to 10
SO_2 Concentration (ppm)	2000 to 9000

Absorber Pressure Drop

Another significant result of the test program was determination of the absorber pressure drop as a function of various absorber operating parameters. Of the parameters which were examined during the test program, only packing depth and gas velocity were found to have a significant impact on the pressure drop in the absorber. Based on theoretical considerations and on measurements made on the pilot absorber, pressure drop was found to be a linear function of packing depth. That is, a doubling in the packing depth results in a doubling of the pressure drop in the absorber.

The relationship between gas velocities and pressure drop is somewhat more complex as illustrated by Figure 1-5. As shown, pressure drop appears to increase exponentially with increasing gas velocity. This is an important consideration in designing an absorber since the gas velocity would be selected based on a trade-off of absorber cross section versus pressure drop. Relatively low gas velocities result in a larger absorber with a lower pressure drop while high gas velocities result in a smaller absorber with a higher pressure drop. The trade-off which must be evaluated is an economic one; the capital costs for a larger absorber versus the operating costs of overcoming a higher pressure drop.

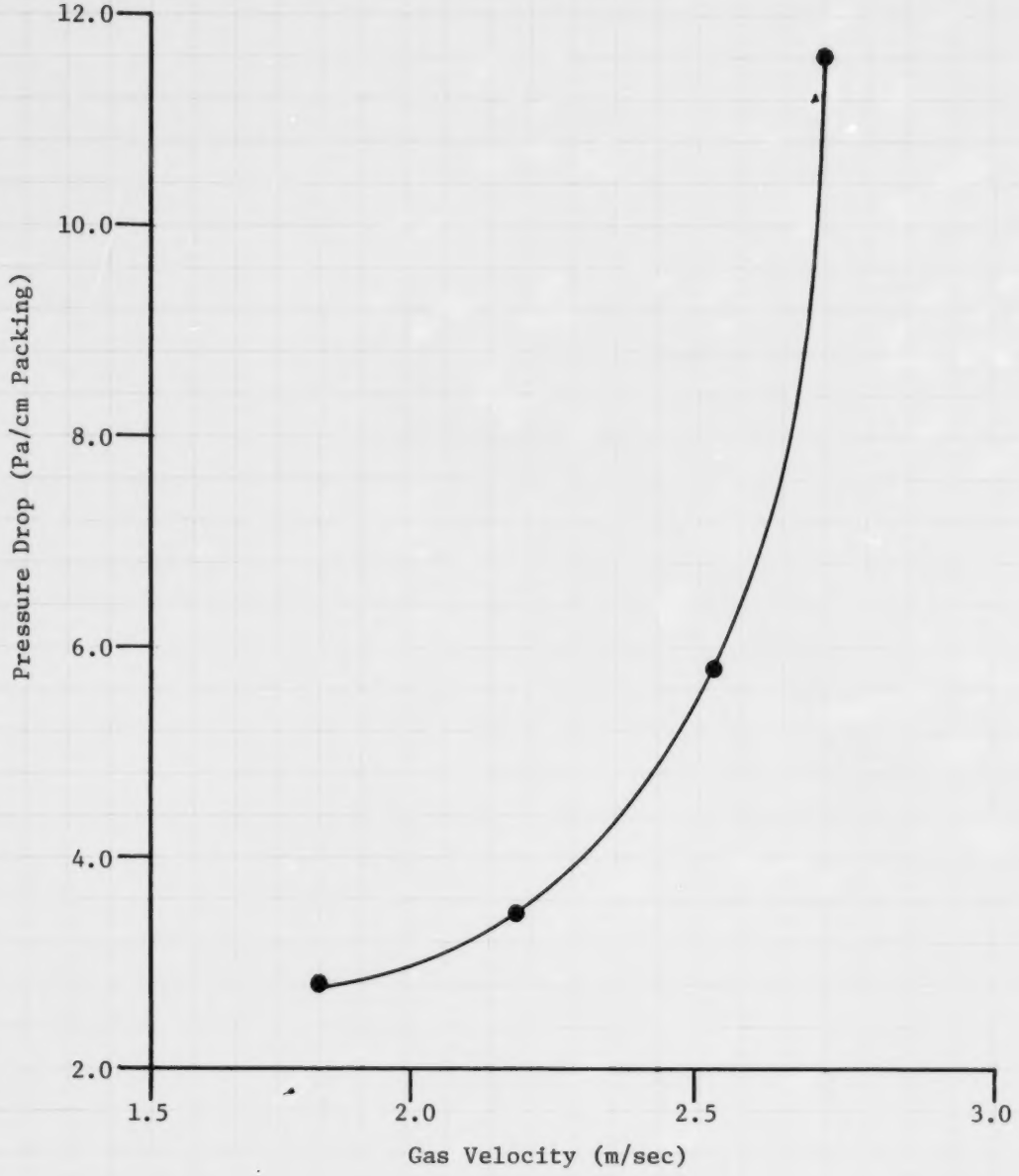

Figure 1-5. Absorber pressure drop as a function of gas velocity.

1.3 CONCLUSIONS AND RECOMMENDATIONS

This section presents major conclusions and recommendations based on an analysis of the results from the Molycorp pilot-scale tests. The data and information developed as part of the study are summarized in Section 4 of this report. These data serve as a basis for the conclusions and recommendations presented here.

Conclusions

The major conclusions of the Molycorp pilot-scale tests are:

1) The MgO scrubbing system which was tested at Molycorp's Washington, Pennsylvania plant was capable of removing over 90 percent of the SO_2 from an off-gas stream containing up to 9000 ppm SO_2. The use of a packed absorber in conjunction with the MgO sorbent was the major factor which contributed to the good system performance. This is due to the high (relative to a spray tower) liquid residence time and overall area for mass transfer which exist in a packed absorber. The long liquid residence time in the absorber helped promote dissolution of $MgSO_3$ solids in the absorber which effectively increased the liquid phase alkalinity of the scrubbing slurry.

2) An equation (Equation 1-4) was developed to correlate the results of the pilot-scale tests. The correlation of experimental data was excellent and the equation can be used to design an MgO absorber using identical packing material treating a gas stream which is similar in composition to the one at Molycorp. In using the design equation, the level of absorber operating parameters should be in the range of parameters examined during the pilot-scale tests (see Table 1-1).

3) For most operating conditions, plugging of the absorber bed was not a problem. However, at very high SO_2 removal efficiencies (>95 percent) $MgSO_3$ solids did begin to accumulate in the absorber. In order to prevent such accumulation, the SO_2 concentration at the outlet of the packed bed should be maintained above 500 ppm. If additional SO_2 removal is required, a clear liquor spray installed above the packing should permit absorber operation without plugging.

4) Process control of the pilot-scale MgO system was not difficult. Measurement of reaction tank pH provided an indicator which could be used to accurately control the $Mg(OH)_2$ feed rate to the system. Also, changes in gas flow rate (over the range tested) did not require any corresponding changes in other absorber operating parameters to maintain a constant SO_2 removal efficiency.

5) Because the pilot unit was not operated as a closed-loop system, there were certain issues which were not addressed during the test program. Of these, it appears that buildup of $MgSO_4$(aq) will have the largest impact on the test results. This is due to the fact that as $MgSO_4$(aq) does build up, $MgSO_3$(aq) solubility will decrease, thus decreasing available liquid phase alkalinity in the scrubbing slurry and possibly decreasing the SO_2 removal efficiency. Theoretically, a decrease in alkalinity can be offset by a corresponding increase in liquid flow rate to the absorber, but tests should be conducted to confirm this fact prior to using the design equation.

6) A comparison of the pilot plant test results to those reported for utility applications of the MgO system indicate that the system tested at Molycorp was generally superior. The Molycorp pilot tests resulted in higher SO_2 removal efficiencies and lower absorber pressure drops than those reported by utility applications. The principal reason for the superior performance is the absorber design used; a packed absorber in the pilot tests vs. a venturi type absorber in the utility systems. In general, the packed absorber appears well suited to treating off-gas streams which contain high concentrations of SO_2 (up to 9000 ppm).

Recommendations

The major recommendation of this study is that, if the MgO system is considered for application to an SO_2 stream containing $\sim$1 percent SO_2, further test work should be conducted at a larger scale. If a large-scale system is considered, the design equation developed during the pilot-scale tests can be used as a basis for designing a system with approximately 10 times the capacity of the pilot unit. Also, any further test work should be conducted on a closed-loop system to verify the expected impact of $MgSO_4$(aq) buildup in the system and to demonstrate the operation of the entire MgO process.

SECTION 2

INTRODUCTION

This report is the result of a research project in which a conventional flue gas desulfurization (FGD) system using magnesium oxide (MgO) scrubbing to process off-gas from a molydenum roaster was tested. The overall objective of the program was to determine the feasibility of applying FGD based on MgO scrubbing to off-gases which are presently uncontrolled sources of SO_2 emissions in the primary nonferrous metals industry.

2.1 BACKGROUND

Processes in the primary nonferrous metals industry produce off-gases containing significant quantities of SO_2. Typically, these streams are classified as "strong" or "weak" depending on their SO_2 concentration. Strong gas streams have SO_2 concentrations greater than 3.5 to 4.0 volume percent while weak gas streams contain between 0.5 and 3.5 volume percent SO_2.

The quantity of SO_2 produced by the primary nonferrous metals industry makes it the second largest potential source of SO_2 emissions in the U.S. However, the strong SO_2 streams are controlled by processing in conventional sulfuric acid plants and the SO_2 concentration can be reduced to 500 ppm or less. This results in control of a large portion of potential SO_2 emissions from primary nonferrous metals processing. Unfortunately, the weak SO_2 streams represent a comparable portion of SO_2 emissions and the principal source of uncontrolled SO_2 emissions in the industry. For example, the major source of SO_2 emissions from primary copper smelters in the U.S. is the reverberatory furnace. SO_2 emitted from the reverberatory furnace averages 22 weight percent of the total sulfur entering the smelter but these

emissions can be as high as 34 percent. Typical SO_2 concentrations in reverberatory furnace off-gases range from 0.4 to 1.5 volume percent SO_2 which is too low to process in a conventional sulfuric acid plant. As a consequence, many of the weak SO_2 streams are currently uncontrolled.

One potential method of controlling weak SO_2 streams is to apply flue gas desulfurization processes. The use of FGD technology to control weak SO_2 streams involves transfer of this technology from the utility industry which has been using these systems for over ten years. FGD processes can convert the sulfur dioxide to several forms. A nonregenerable solid waste may be produced (e.g., $CaSO_4$) or a regenerable process may be used to produce a concentrated SO_2 stream which can be further processed to sulfuric acid or elemental sulfur. Because of the difference in gas stream characteristics, particularly the SO_2 concentrations which are 2 to 5 times that encountered in utility applications, many uncertainties are involved in applying the current state-of-the-art FGD technology to weak SO_2 off-gases in the primary nonferrous metals industry.

EPA's Program

As part of the Environmental Protection Agency's continuing research and development efforts, the Industrial Environmental Research Laboratory in Cincinnati, Ohio, has sponsored a test program to investigate the performance of a "conventional" FGD system processing a weak SO_2 stream. The prime contractor in this test program was Molycorp Inc. The testing took place at Molycorp's Washington, Pennsylvania plant and Molycorp was responsible for installation and maintenance of a skid-mounted pilot scrubber. Radian Corporation, as a subcontractor, supplied the pilot scrubber. Radian also conducted the test program, provided sampling and analysis support, and was responsible for evaluation of the results of the test program.

The FGD system tested was a magnesia (M_gO) slurry scrubbing process. This system was selected for testing for several teasons. First, the M_gO

system appeared promising because it has been successfully applied to treat approximately 90,000 Nm^3/hr of reverberatory furnace off-gas (2 or 3 percent SO_2) in Japan. Also, the by-product of MgO scrubbing is a concentrated (approximately 10 percent) SO_2 stream which can be processed in a sulfuric acid plant.

2.2 OBJECTIVES AND APPROACH

The test program had two primary objectives:

- Provide preliminary performance testing of the MgO FGD process on a weak SO_2 off-gas stream.
- Develop data for the MgO system which could be used to design an absorber for treating similar gas streams and scale-up to the next size increment.

In examining the MgO system, performance data of interest included the SO_2 removal attainable as a function of process operating parameter levels, the type of solid by-product produced, and the rate of SO_2 oxidation in the absorber. The design data collected during the test program included absorber size as a function of off-gas flow rate, absorber liquid feed rate, and absorber pressure drop.

SECTION 3

TEST PROGRAM

During June through September 1979, Radian Corporation conducted pilot-scale tests of the MgO slurry scrubbing process. These tests were conducted at Molycorp's Washington, Pennsylvania plant treating the off-gas from a molybdenum disulfide roaster. Gas flow rates through the pilot scrubber ranged from 2800 to 4000 Nm^3/hr (1700-2600 scfm). The SO_2 concentration of the gas at the scrubber inlet was typically 7000 to 8000 ppm while the removal ranged from 43 to 98 percent depending on the test conditions. The test program conducted during this period examined a range of important independent variables.

This section presents details of the test program conducted at Molycorp's plant. Included as background are a discussion of the MgO scrubbing process and chemistry and a description of the pilot scrubbing system used during the test program.

3.1 MgO PROCESS DESCRIPTION

The MgO FGD process was originally developed for use in the pulp and paper industry but recent development efforts in the U.S. have focused on utility industry applications. In fact, there have been three commercial-scale MgO systems installed on power plant boilers in the U.S.[2] Two of these were demonstration units and their operation has since been terminated. The third unit is currently operated commercially on a 120 MWe coal-fired power plant. In addition to these units, the MgO process reportedly has been successfully applied to a reverberatory furnace in Japan. This system was installed at the Onahama copper smelter in 1972 and has operated for several

years.[1] However, it has ceased operation because of the oversupply of sulfuric acid and a more favorable demand for gypsum (wallboard), a by-product of the alternative lime scrubbing system now used.

Figure 3-1 is a schematic of a "typical" utility application of the MgO process. As shown, flue gas is treated in a venturi prescrubber for particulate and chloride removal prior to entering the absorber. This is necessary due to the closed-loop operation of the process. Since MgO is recycled, impurities entering the scrubbing loop are not purged. In a utility application, the buildup of chloride can cause considerable corrosion problems if it is not removed in the prescrubber.

Once cleaned of particulates and saturated, the gas enters the absorber where it is contacted with a recirculating slurry which contains solid and dissolved $MgSO_3$. Smaller amounts of MgO and $MgSO_4$ may also be present. In the absorber, the following reaction results in removal of SO_2.

$$SO_2(g) + H_2O(\ell) \rightleftarrows H_2SO_3(aq) \qquad (3\text{-}1)$$

Since water has only a limited capacity for SO_2 absorption, the high removal efficiency of the MgO process results from the alkalinity provided by $MgSO_3$ as shown in Equation 3-2.

$$H_2SO_3(aq) + MgSO_3(aq) \rightleftarrows Mg(HSO_3)_2(aq) \qquad (3\text{-}2)$$

As this reaction proceeds to the right, the vapor pressure of SO_2 over the scrubbing slurry is lowered and more SO_2 sorption can occur. It should be noted that the reaction represented by Equation 3-2 is actually an ionic reaction (*i.e.*, $H_2SO_3 + SO_3^{=} \rightleftarrows 2HSO_3^{=}$). However, in the interest of clarity, this and subsequent equations represent ionic reactions as molecular.

Another reaction which occurs in the absorber and contributes to the SO_2 sorption capacity of the scrubbing slurry is illustrated by Equation 3-3.

$$MgSO_3 \cdot 6H_2O(s) \rightleftarrows MgSO_3(aq) + 6H_2O \qquad (3\text{-}3)$$

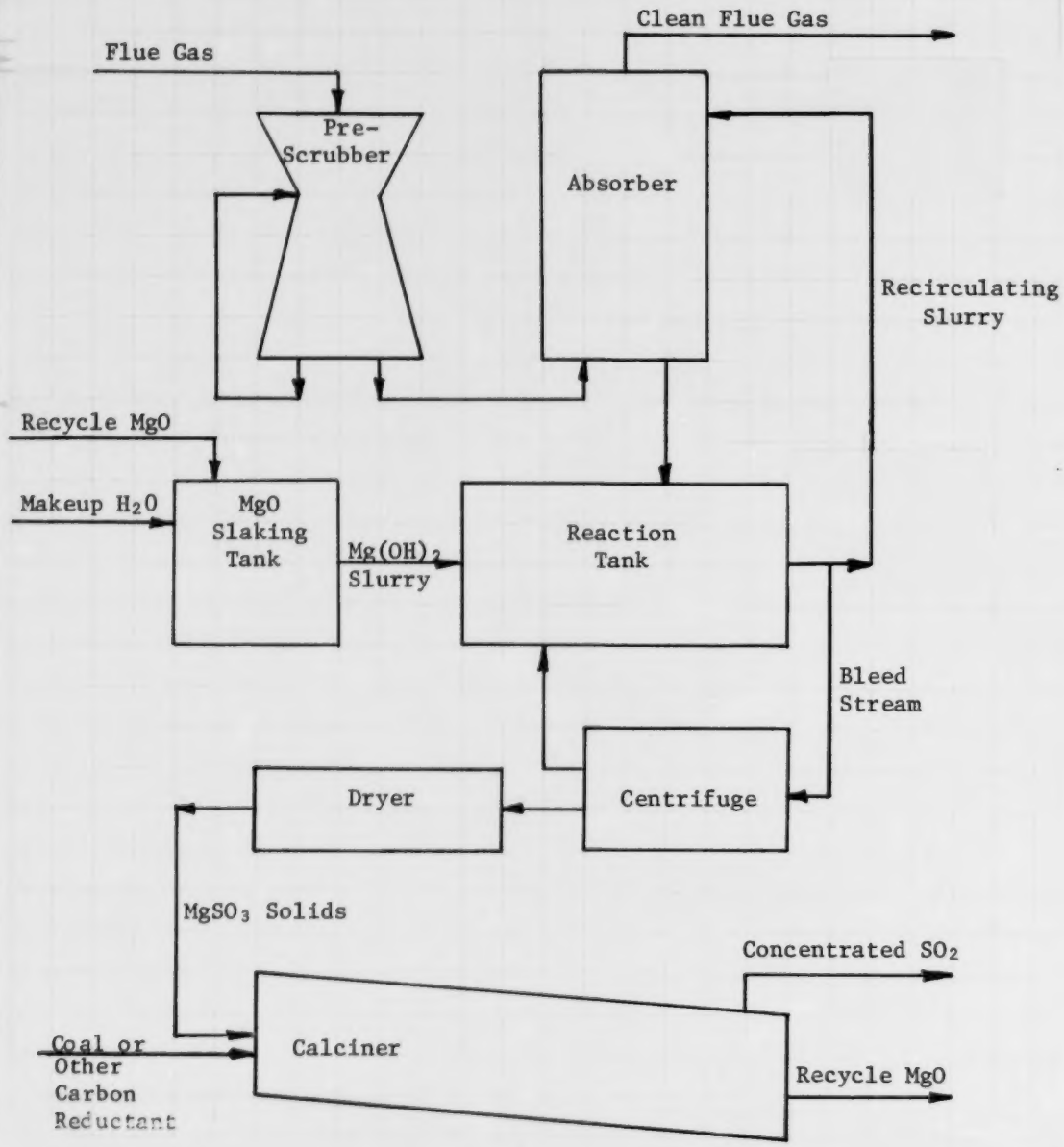

Figure 3-1. Schematic of typical utility MgO system.

As the reaction shown in Equation 3-2 proceeds to the right, the concentration of aqueous $MgSO_3$ is reduced and a driving force for the dissolution of $MgSO_3 \cdot 6H_2O$ solids exists. This permits the reaction shown in Equation 3-3 to proceed as written. It should be noted that solid $MgSO_3$ can exist as either the tri- or the hexahydrate. The hexahydrate is shown in the equations here since that was the predominant form found during the pilot plant tests. A discussion of the factors which determine which hydrate will form is presented in Section 4.

The slurry which exits the absorber is at a lower pH than the absorber feed and most of the aqueous phase sulfite is present as HSO_3^-. This slurry then enters a reaction tank where the pH is raised by addition of $Mg(OH)_2$ slurry. The increase in pH results in a shift from HSO_3^- to $SO_3^=$ as shown in Figure 3-2 and illustrated by Equation 3-4.

$$Mg(OH)_2 + Mg(HSO_3)_2 \rightleftarrows 2MgSO_3(aq) + 2H_2O \qquad (3\text{-}4)$$

This reaction results in the production of two moles of $MgSO_3(aq)$ for each mole of $Mg(HSO_3)_2(aq)$ initially present. As a consequence, the slurry in the reaction tank becomes supersaturated with respect to $MgSO_3(aq)$ and the reaction shown in Equation 3-3 proceeds in the reverse direction as shown in Equation 3-5.

$$MgSO_3(aq) + 6H_2O \rightleftarrows MgSO_3 \cdot 6H_2O(s)\downarrow \qquad (3\text{-}5)$$

This results in the production of magnesium sulfite solids at a molar rate equivalent to the SO_2 removal in the absorber (*i.e.*, the number of moles of $MgSO_3$ which precipitate equals the number of moles of SO_2 removed in the absorber).

The reaction tank is sized such that the reaction shown in Equation 3-5 approaches equilibrium. This is necessary to prevent precipitation of solid $MgSO_3$ in the absorber. While $MgSO_3$ solids or "scale" are not difficult to

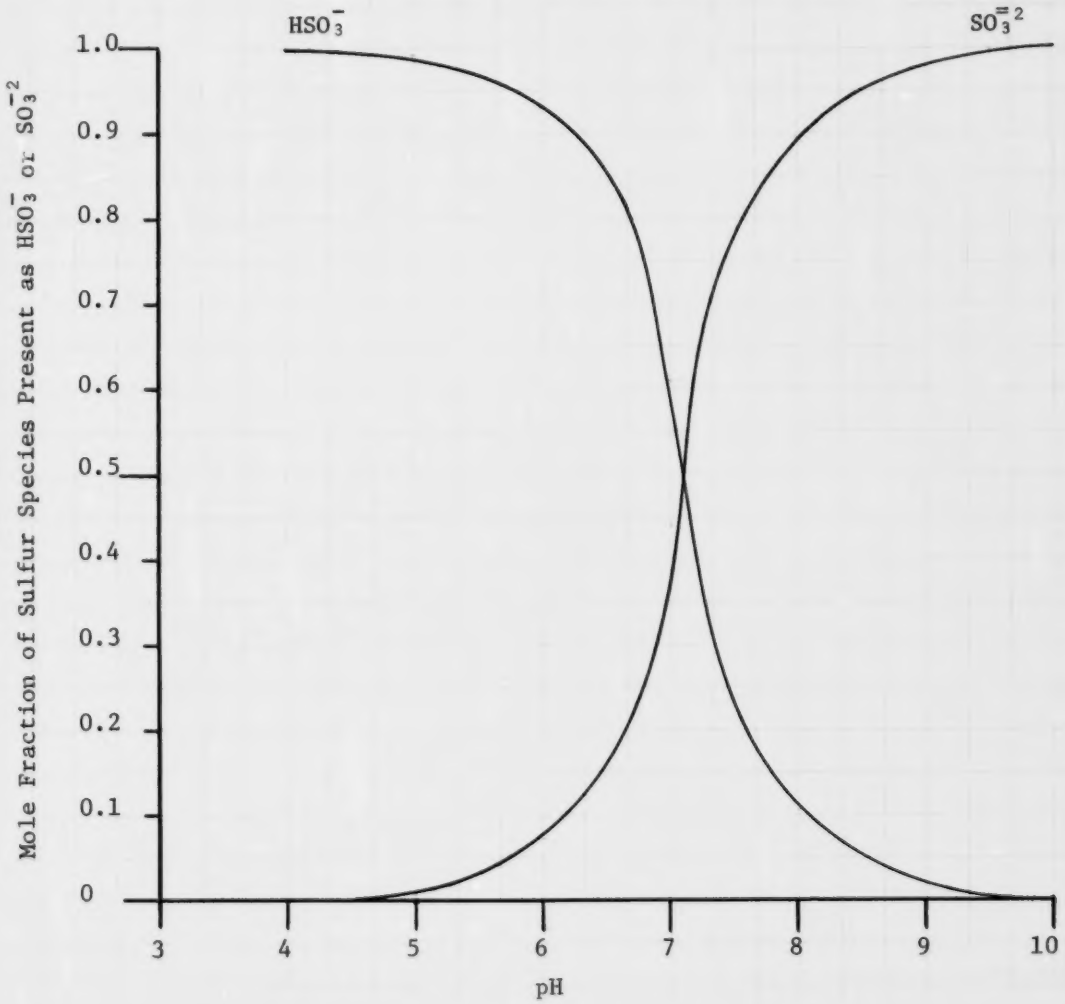

Figure 3-2. Relative fractions of HSO_3^- and $SO_3^=$ as a function of pH.

remove, formation in the absorber can result in forced outages to permit cleaning of such deposits.

Slurry from the reaction tank is recycled to the absorber and a bleed stream is removed for regeneration. The rate at which slurry is removed in the bleed stream is determined by the quantity of SO_2 removed in the absorber. The number of moles of $MgSO_3 \cdot 6H_2O$ in the bleed stream must equal the number of moles of SO_2 removed from the gas stream in the absorber. This results in the same quantity of MgO being regenerated as is consumed in the reaction tank. Of course, the regeneration step can be decoupled from the absorption step, provided surge capacity exists for $MgSO_3$ and MgO storage.

The bleed stream removed from the absorber loop is first dewatered, typically in a centrifuge. The hydrated $MgSO_3$ solids from the centrifuge are then processed in a dryer where the water of hydration is removed as illustrated by Equation 3-6.

$$MgSO_3 \cdot 6H_2O(s) \xrightarrow{\Delta} MgSO_3(s) + 6H_2O(g) \qquad (3\text{-}6)$$

The dehydrated $MgSO_3$ solids from the dryer are then routed to a calciner. In the calciner MgO is regenerated and a concentrated SO_2 stream is produced. This regeneration reaction is illustrated by Equation 3-7.

$$MgSO_3(s) \xrightarrow{\Delta} MgO(s) + SO_2(g) \qquad (3\text{-}7)$$

The temperature required for this reaction to proceed ranges from 400 to 1000°C.

In addition to regeneration of $MgSO_3$, the calcination step can be used to regenerate any $MgSO_4$ produced in the process. $MgSO_4$ is produced in the absorber by oxidation of aqueous sulfite ions as shown in Equation 3-8 or by absorption of SO_3 from the flue gas.

$$MgSO_3(aq) + \tfrac{1}{2}O_2(g) \rightarrow MgSO_4(aq) \qquad (3\text{-}8)$$

In addition, $MgSO_4$ can be produced as a result of air oxidation of $MgSO_3$ solids at any point in the process prior to regeneration.

In order to regenerate $MgSO_4$, carbon in the form of coke is added to the calciner and a reducing atmosphere is produced. The overall reaction for $MgSO_4$ regeneration is shown in Equation 3-9.

$$MgSO_4(s) + C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g) + MgO(s) + SO_2(g) \qquad (3\text{-}9)$$

The MgO product from the calciner is recycled to the system where it is slaked and then fed to the reaction tank.

Off-gas from the calciner contains approximately 10 volume percent SO_2. This gas stream is suitable for processing in a sulfuric acid plant. The three utility applications and the copper smelter in Japan have all produced sulfuric acid as the end product of the MgO process.

3.2 PILOT PLANT DESCRIPTION

The operation of the magnesium slurry scrubbing process is complex and involves several processing steps including:

- absorption,
- solids separation and handling, and
- regeneration.

The nature of the process is such that the solids handling and regeneration steps are substantially independent of the absorption process. While this is not strictly true, once the type of solids produced (tri- or hexahydrate) are identified, the solids handling and regeneration equipment can be designed independently of the absorber. For this reason, the test program conducted at Molycorp's plant focused on characterization of absorber operation and the type of solids produced.

Figure 3-3 is a schematic of the pilot unit installed at Molycorp's plant. As shown, the pilot unit consisted of an absorber, reaction tank, and solids separator. For the purpose of these brief tests, the solids produced were disposed of by ponding rather than being dryed and regenerated.

The absorber was a 76 cm (30 inch) diameter tower containing two beds of 2.5 cm (1 inch) tellerette packing (Figure 3-4). The upper bed depth was 76 cm (30 inches) and the lower bed was 51 cm (20 inches) deep. The piping and valve arrangement was designed to distribute slurry through both beds or the lower bed only. This permitted scrubbing tests at packing depths of 51 cm (20 inches) and 127 cm (50 inches). Full cone spray nozzles were used for liquid distribution and were arranged so that the edge of the spray contacted the tower wall at the level of the packing.

Gas flow rates through the absorber ranged from 2800 to 4000 Nm^3/hr (1700 to 2600 scfm) while slurry flow rates ranged from 0.4 to 2.4 ℓ/sec (6 to 38 gpm). During most tests, the pH of the absorber feed was maintained between 7.5 and 8.0. Slurry exiting the absorber was gravity-fed to a 5680 ℓ (1500 gallon) reaction tank. The pH of the slurry leaving the absorber ranged from 4.5 to 6.5 and $Mg(OH)_2$ was added to the reaction tank to raise the pH back to 7.5-8.0.

The scrubbing slurry contained 4 to 8 weight percent $MgSO_3 \cdot 6H_2O$ solids. A bleed stream of slurry was removed from the reaction tank and concentrated to approximately 35 weight percent solids in a clarifier. Overflow from the clarifier was either returned to the reaction tank or used to slurry fresh $Mg(OH)_2$ which was fed to the reaction tank. Makeup water was also added to the $Mg(OH)_2$ slurry tank.

Test Plan

A test plan was designed to evaluate the performance of the pilot-scale absorber using MgO slurry to treat pre-cleaned off-gas from the molybdenum roaster. The design of the test plan required identification of the important

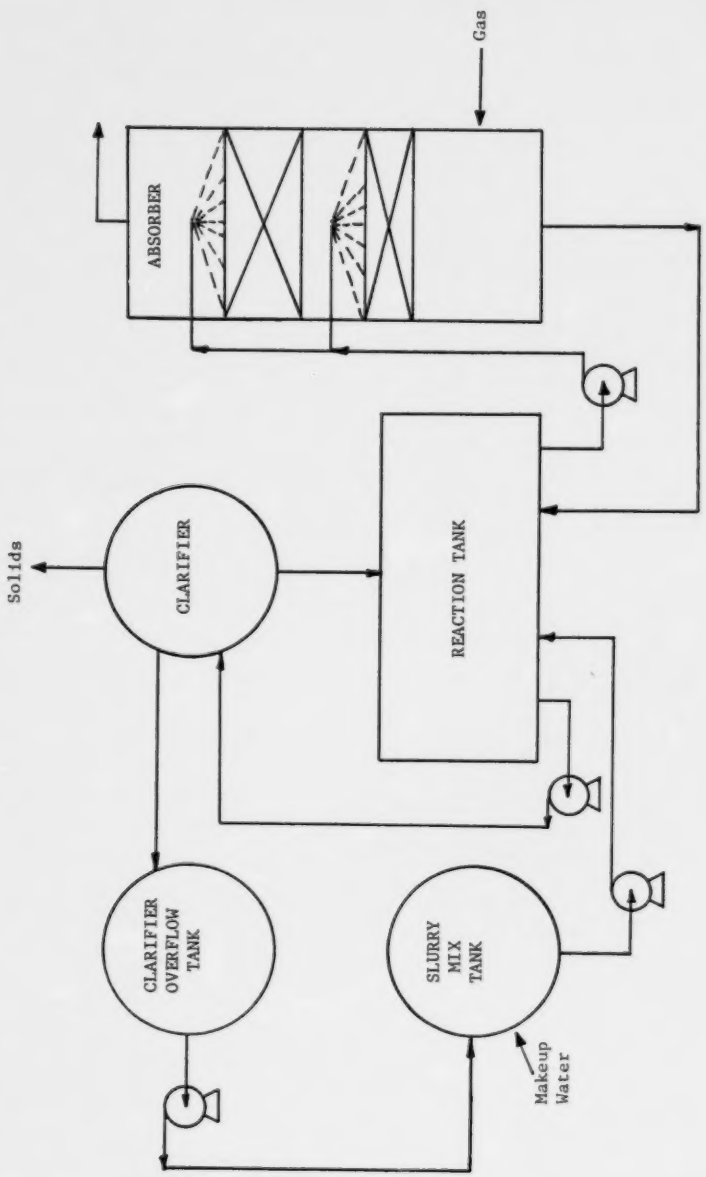

Figure 3-3. Schematic of Molycorp pilot unit.

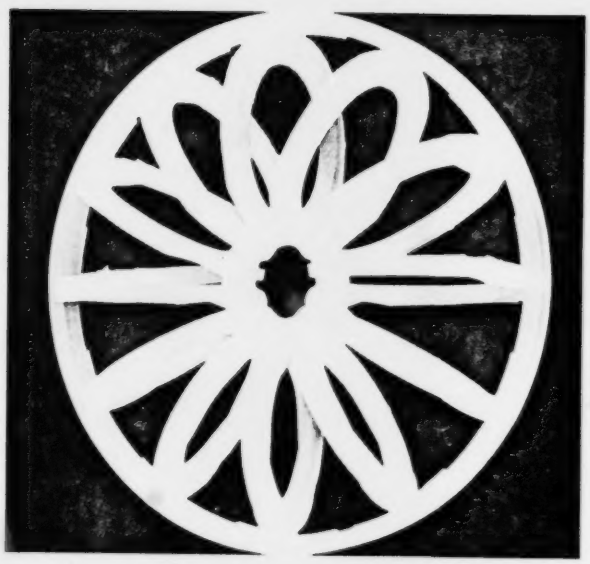

Figure 3-4. Telleretta absorber packing material; actual size - 2.5cm (1 inch).

independent variables and then systematically changing these variables over a range consistent with the absorber design. Variables of principal interest are:

- liquid-to-gas ratio (L/G),
- gas flow rate, and
- packing depth.

Characterization of absorber performance as a function of these variables should permit selection of an optimum design for an absorber treating a similar gas stream.

The test plan developed to examine these variables is shown in Table 3-1. This test plan was a 3x3x2 factorial design. In other words, the tests examined all possible combinations of two packing depths, three gas flow rates, and three L/Gs. These test conditions were selected to represent a reasonable range of absorber operating conditions.

Another important independent variable is pH. This variable was not included in the test matrix shown in Table 3-1 for several reasons. First, addition of a fourth variable to the test matrix will double (for two pH levels) or triple (for three levels) the number of tests required for a full factorial design. Second, previous development work has determined that the optimum pH for MgO scrubbing is in the range of 7.0 to 8.0.[5,6] For these reasons, all the tests shown in Table 3-2 were conducted at pH levels in the range 7.0 to 8.0. Only a limited number of tests were conducted at pH levels outside this range. Test conditions for pH variations are presented in Table 3-2. The levels for packing depth, gas flow rate, and L/G maintained during the pH tests were selected to maximize the effects of changing pH on SO_2 removal.

Another variable which was examined during a limited number of tests was the inlet SO_2 concentration of the flue gas. While this is not typically an independent variable, the SO_2 concentration is known to impact the rate of mass transfer and thus SO_2 removal in the absorber. Conditions for the SO_2

TABLE 3-1. INDEPENDENT VARIABLE TEST PLAN FOR MgO PILOT TESTS

Variable Level							
L/G		Gas flow rate		Packing depth			SO_2 Concentration
(ℓ/Nm^3)	(gal/1000 scf)	(Nm^3/hr)	(scfm)	(cm)	(in)	pH	(ppm)
0.71	5	2800	1750	51	20	7.5	As received from roaster
1.41	10	2800	1750	51	20	7.5	
2.12	15	2800	1750	51	20	7.5	
0.71	5	3380	2100	51	20	7.5	
1.41	10	3380	2100	51	20	7.5	
2.12	15	3380	2100	51	20	7.5	
0.71	5	4000	2500	51	20	7.5	
1.41	10	4000	2500	51	20	7.5	
2.12	15	4000	2500	51	20	7.5	
0.71	5	2800	1750	127	50	7.5	
1.41	10	2800	1750	127	50	7.5	
2.12	15	2800	1750	127	50	7.5	
0.71	5	3380	2100	127	50	7.5	
1.41	10	3380	2100	127	50	7.5	
2.12	15	3380	2100	127	50	7.5	
0.71	5	4000	2500	127	50	7.5	
1.41	10	4000	2500	127	50	7.5	
2.12	15	4000	2500	127	50	7.5	

concentration tests are also shown in Table 3-2. Again, the levels of other independent variables were selected to maximize the impacts of changing SO_2 concentration.

TABLE 3-2. CONDITIONS FOR pH AND SO_2 CONCENTRATION TESTS

L/G (ℓ/Nm)	Packing depth (cm)	Gas flow rate (Nm^3/hr)	pH	SO_2 concentration (ppm)
0.71	127	4000	6.5	As Received
0.71	127	4000	5.5	As Received
0.71	127	4000	7.5	6000
0.71	127	4000	7.5	4000
0.71	127	4000	7.5	2000

In total, 23 parametric tests were included in the test program. These tests were scheduled to be followed by a steady-state or duration test (approximately 5 days) to permit collection of data so material balances could be completed for the pilot unit. The conditions for this duration test were not selected prior to the test program but were to be determined based on the results of the parametric tests.

During the test program, the pilot unit was operated at a specified set of test conditions until the SO_2 removal stabilized, as demonstrated by monitoring outlet SO_2. This usually required about one half hour. At that point, slurry samples were taken from the absorber feed and absorber bottoms and analyzed for the parameters shown in Table 3-3. The liquor concentration was still changing slowly when samples were taken, but the changes did not affect SO_2 removal. Stabilization of the liquor concentration would have required several days operation. Details of the analytical procedures used during the test program are presented in Appendix A. In addition to sampling and chemical analyses, process measurements were recorded during each test. These measurements are shown in Table 3-4. A DuPont Model 400 photometric analyzer was used for measurement of SO_2. The analyzer readings were checked periodically by manual measurement using the Reich test (see Appendix A for details). The pH of the reaction tank was continuously monitored and recorded.

TABLE 3-3. PARAMETERS MEASURED BY CHEMICAL/PHYSICAL ANALYSIS

Stream component	Parameter measured
Slurry	pH wt % solids Temperature
Aqueous Phase	Mg^{++} $SO_3^=$ Total Sulfur Cl^- $CO_3^=$
Solid Phase	Mg^{++} $SO_3^=$ Total Sulfur

TABLE 3-4. PROCESS MEASUREMENTS FOR THE PILOT ABSORBER

Stream	Measurement
Inlet Flue Gas	Flow rate Temperature Pressure SO_2 Concentration
Outlet Flue Gas	Temperature Pressure SO_2 Concentration
Scrubber Feed	Flow rate
Reaction Tank	Temperature pH

SECTION 4

PILOT PLANT TEST RESULTS

Conditions for the pilot-scale tests were based on the test plan presented in Section 3 of this report. The results of these tests quantify the relationship between dependent variables, principally SO_2 removal and absorber presure drop, and the independent variables tested.

This section presents the relationships developed as a result of the pilot-scale test program including a mathematical model of the absorber's performance. The model was developed based on theoretical considerations and is used to correlate the test results. In addition, other results of the test program are presented in this section including:

- $SO_3^=$ oxidation in the absorber,
- type of solids produced, and
- process control requirements.

Finally, the results of the pilot-scale tests are compared to the results of previous tests of the MgO system and issues not addressed during the pilot program are discussed.

4.1 SHORT-TERM VARIABLE TESTS

A total of 23 short-term variable tests were scheduled as part of the test plan developed for this study. As a result of some duplication and addition of tests at selected conditions, 30 tests were conducted. The duration of these tests ranged from 2 to 4 hours and was dependent on the time required for lineout of gas and liquid rates in the absorber (since SO_2

removal would not stabilize until the gas and liquid rates were stabilized) and the time required to obtain samples for chemical analysis. Operation of the roaster also affected test duration since changes in roaster operating conditions could affect the inlet SO_2 concenctration. If such changes were made at the start of a test, more time was required for the gas and liquid rates and SO_2 removal to stabilize so sampling could begin. Once samples were obtained, test conditions were changed and the system was allowed to equilibrate before another set of samples was taken.

Table 4-1 presents some of the raw data from the 23 scheduled variable tests and compares the planned and actual test conditions. The tests were not conducted in the order shown, but were randomized. This was done to prevent biasing the results due to an unforeseen variable effect that theoretically could have occurred (*e.g.*, buildup of $MgSO_4$ in the system). No such variable effect was observed during the tests; the $MgSO_4$ concentration was reasonably stable.

As shown in Table 4-1, the actual test conditions are generally close to those specified in the test plan. However, in some cases the actual conditions vary significantly from the planned conditions. For example, in tests 16, 17, and 18 the planned L/G's ranged from 0.71 to 2.12 while actual L/G's ranged from 0.53 to 1.22. The reason for this discrepancy is that at the conditions of these tests, SO_2 removals were very high and the planned tests at L/G's above 1.22 did not produce useful data. Therefore, test conditions were adjusted based on the performance of the absorber.

Seven tests were conducted to supplement the planned tests shown in Table 4-1. The conditions for these tests are presented in Table 4-2. Test 24 was conducted to determine removal at a higher gas rate. Tests 25, 26, and 27 were conducted to supplement the tests conducted at 4000 Nm^3/hr so the behavior of SO_2 removal as a function of L/G could be better defined. Test 28 examined the impact of reduced pH at conditions which were expected to maximize any impact. Tests 29 and 30 are replicates of test 16. These replicate tests were conducted to provide a more accurate baseline for the

TABLE 4-1. PLANNED AND ACTUAL CONDITIONS FOR THE MOLYCORP MgO TEST PROGRAM

Test No.	L/G (ℓ/Nm³)		Gas flow rate (Nm³/hr)		pH		SO_2 concentration (ppm)		Packing Depth (cm)	SO_2 Removal (%)
	Planned	Actual	Planned	Actual	Planned	Actual	Planned	Actual		
1	0.71	0.66	2800	2700	7.5	7.8	-	8670	51	44
2	1.41	1.25	2800	2850	7.5	7.7	-	7410	51	57
3	2.12	1.95	2800	2840	7.5	7.8	-	7460	51	68
4	0.71	0.61	3380	3380	7.5	8.0	-	8200	51	43
5	1.41	1.28	3380	3360	7.5	7.8	-	8090	51	65
6	2.12	2.03	3380	3390	7.5	7.8	-	8200	51	71
7	0.71	0.59	4000	3910	7.5	7.7	-	8050	51	49
8	1.41	1.33	4000	3910	7.5	7.9	-	8310	51	66
9	2.12	1.78	4000	3910	7.5	7.8	-	7840	51	76
10	0.71	0.49	2800	2850	7.5	8.0	-	8760	127	73
11	1.41	1.18	2800	2850	7.5	7.8	-	8120	127	88
12	2.12	1.76	2800	2850	7.5	7.7	-	7820	127	96
13	0.71	0.53	3380	3370	7.5	8.0	-	6230	127	77
14	1.41	0.89	3380	3390	7.5	8.0	-	7620	127	95
15	2.12	1.21	3380	3360	7.5	7.9	-	8510	127	98
16	0.71	0.53	4000	4000	7.5	7.8	-	7990	127	79
17	1.41	0.99	4000	3890	7.5	7.7	-	8470	127	95
18	2.12	1.22	4000	3910	7.5	7.7	-	8080	127	97
19	0.71	0.55	4000	3910	6.5	6.6	-	8590	127	55
20	0.71	0.55	4000	3900	5.5	5.8	-	6880	127	44
21	0.71	0.55	4000	3910	7.5	8.1	6000	6030	127	92
22	0.71	0.55	4000	3910	7.5	8.0	4000	4610	127	95
23	0.71	0.55	4000	3910	7.5	8.0	2000	2350	127	96

TABLE 4-2. CONDITIONS AND RESULTS OF ADDITIONAL PILOT TESTS

Test Number	L/G (ℓ/Nm^3)	Gas flow rate (Nm^3/hr)	pH	SO_2 concentration (ppm)	Packing Depth (cm)	SO_2 Removal (%)
24	1.45	4221	7.9	8090	127	98
25	0.83	3920	7.8	8670	51	54
26	2.23	3910	7.9	7750	51	94
27	0.80	3910	7.8	9260	127	91
28	1.95	2840	6.6	9890	51	54
29	0.55	3910	8.0	9190	127	78
30	0.55	3910	8.0	8200	127	81

pH and SO_2 concentration tests which had identical conditions of L/G, gas flow rate, and packing depth.

The results of the short-term variable tests quantify the relationship between the independent variables tested and the SO_2 removal in the absorber. The following discussion describes the qualitative relationships between the independent variables and SO_2 removal while the subsequent section presents a theoretical and quantitative description of those relationships.

4.1.1 Qualitative Discussion of Test Results

The following variables were examined during the pilot test program:

- L/G ratio,
- gas flow rate,
- packing depth,
- pH, and
- SO_2 concentration.

A discussion of how each of these variables impact the SO_2 removal efficiency in the absorber is presented below.

L/G Ratio--

The liquid-to-gas ratio is a relative measure of the quantity of sorbent fed to the absorber per unit volume of gas treated. Increasing the L/G ratio makes more sorbent available for SO_2 removal so the removal should increase. This is exactly the behavior observed during the pilot tests.

An increase in L/G from a low ($\sim$0.71 ℓ/Nm^3) to intermediate ($\sim$1.41 ℓ/Nm^3) level produced a relatively large increase in SO_2 removal efficiency while a further increase to a high ($\sim$2.12 ℓ/Nm^3) L/G produced a smaller increase in removal efficiency. These results are generally as expected since providing more sorbent increases the capacity for SO_2 removal. However, the effect of increasing the quantity of sorbent on removal efficiency begins diminishing as other factors (*e.g.*, packing depth), start limiting the capacity for SO_2

absorption. The results of the test program also indicate that the L/G ratio has very little effect on the pressure drop across the absorber in the pilot unit for the liquid and gas rates tested.

Gas Flow Rate--

A change in gas flow rate through a packed tower has two opposing effects on removal efficiency. An increase in flow rate increases the quantity of SO_2 which enters the absorber. For a constant liquid flow rate, this would tend to decrease removal efficiency since the L/G ratio would decrease. Therefore, if the L/G ratio is maintained at a constant level, an increase in gas flow rate should not produce a decrease in removal efficiency.

The experimental results confirm that at constant L/G, an increase in gas flow rate does not produce a decrease in removal efficiency. In fact, the test results show that removal efficiency actually improves under these circumstances. This is due to an increase in the overall mass transfer interfacial area term ($K_g a$) which results from the increased gas flow.

Furthermore, over the range of gas flow rates tested during the program, the results indicate that a change in gas flow rate at constant liquid rate has no significant effect. In other words, the effect of a decrease in L/G ratio was offset by an increase in mass transfer. As a result, removal was determined to be independent of gas flow rate over the range of flow rates tested.

An increase in gas flow rate also causes the absorber pressure drop to increase. In fact, the gas flow rate had the most significant influence on pressure drop through the absorber in the range of variables tested.

Packing Depth--

A change in packing depth was found to have a significant impact on removal efficiency as expected. By increasing the packing depth, the area available for transfer of SO_2 from the gas to the scrubbing slurry is increased and, consequently, removal efficiency increases. In addition, the

pressure drop through the absorber was found to increase proportionally with an increase in packing depth.

pH--

The pH of scrubbing slurry is a measure of the ability of the slurry to absorb and react with SO_2. In the case of the pilot-scale MgO system, pH was found to have a significant influence on the ability of the slurry to sorb SO_2. In the pH range tested, a change in pH corresponds almost directly to a change in the $MgSO_3$(aq) concentration (see Figure 3-2). By increasing the pH (through addition of $Mg(OH)_2$), $MgHSO_3$(aq) is converted to $MgSO_3$ which can then react with absorbed SO_2. As expected, an increase in pH results in an increase in SO_2 removal.

SO_2 Concentration--

The SO_2 concentration of a gas stream is not typically an independent variable. However, during the pilot-scale tests at Molycorp, provisions existed to vary the inlet SO_2 concentration by dilution with air. An increase in SO_2 concentration brings more SO_2 into the absorber. At constant conditions of L/G, gas flow rate, packing depth, etc., this would be expected to cause a decrease in removal efficiency. In general, the results of the pilot-scale tests confirm these expectations. However, the test results showed that at lower SO_2 concentrations (2000 ppm), no change was seen in the removal efficiency with varied inlet concentrations. This indicates that at the lower SO_2 concentrations, some other factor (*e.g.*, packing depth) limits the maximum removal efficiency which can be attained.

4.1.2 Quantitative Discussion of Test Results

One of the primary objectives of the pilot-scale test program was to quantify the performance of the absorber as a function of the independent variables tested. In order to meet this objective it was necessary to develop a relationship which correlates SO_2 removal as a function of absorber operating parameters. Conventional absorption theory usually presents a general form for such a correlation. By applying statistical analysis to the test

results, it is possible to determine empirical constants and develop an expression which quantifies SO_2 removal as a function of absorber operating parameters. The following discussion examines conventional absorption theory, presents the general form for the SO_2 removal relationship, and presents and examines the results of a statistical analysis of the test data.

Absorption Theory--

The removal of SO_2 from a gas stream involves vapor-liquid mass transfer followed by chemical reaction. The ability of absorption theory to describe this phenomenon is limited to the vapor-liquid mass transfer phenomena. The addition of the chemical reaction term complicates the discussion and is best treated by an empirical approach. Therefore, in developing a general relationship for SO_2 removal as a function of absorber design and operating parameters, only vapor-liquid mass transfer will be considered.

The traditional basis for the analysis of vapor-liquid mass transfer phenomena is the two-film theory in which the total resistance to mass transfer is expressed as the sum of individual resistances in the vapor and liquid phases near their interface. Using this approach, the molar flux of component A (N_A) from the gas to the liquid phase can be expressed by Equations 4-1 and 4-2.

$$N_A = k_g P(Y_A - Y_{Ai}) (\text{mole/cm}^2\text{-sec}) \qquad (4\text{-}1)$$

$$N_A = k_\ell (C_{Ai} - C_A) (\text{mole/cm}^2\text{-sec}) \qquad (4\text{-}2)$$

where k_g (mole/cm -sec-unit driving force) and k_ℓ are individual gas and liquid phase mass transfer coefficients. Here, Y_A is the bulk gas phase mole fraction of component A, Y_{Ai} is the interfacial gas phase mole fraction of A, P is the total pressure, and C_A and C_{Ai} are the corresponding concentrations of A in the bulk liquid and at the liquid interface. The transfer of A from the gas to the liquid is depicted graphically in Figure 4-1.

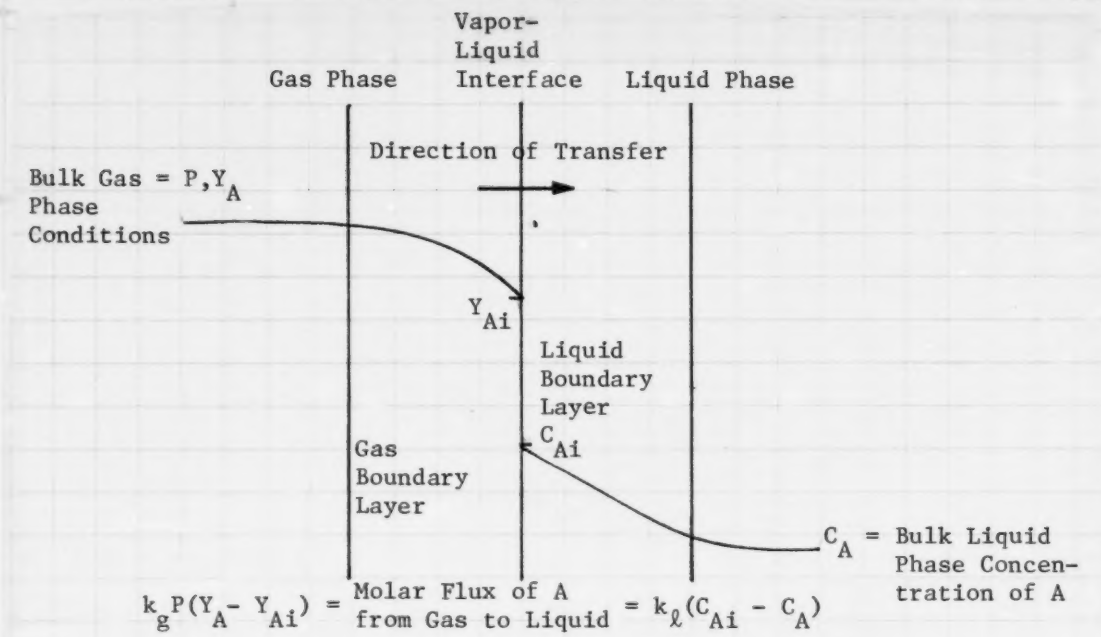

Figure 4-1. Schematic representation of two-film theory for mass transfer.

Now, if Henry's Law applies, as it does for most physically dissolved, slightly soluble gases, then a linear relationship exists between the equilibrium gas and liquid phase concentrations of component A. This relationship is shown in Equation 4-3.

$$PY_A^* = HC_A \tag{4-3}$$

Here, H is the Henry's Law constant, and Y_A^* is the gas phase mole fraction of component A which is in equilibrium with a liquid having a composition C_A.

If the vapor-liquid interface is assumed to be at equilibrium, the application of Henry's Law to the mass transfer situation shown in Figure 4-1 yields the following relationship.

$$PY_{Ai} = HC_{Ai} \tag{4-4}$$

Equations 4-1 through 4-4 can be combined to yield Equation 4-5.

$$N_A = \left(\frac{1}{k_g} + \frac{H}{k_\ell}\right)^{-1} P\ (Y_A - Y_A^*)(\text{mole/cm}^2\text{-sec}) \qquad (4\text{-}5)$$

If a chemical reaction is involved, as in SO_2 dissolution, the solubility relationship for Y_A^* is nonlinear and much more complex than that indicated in Equation 4-3. For purposes of developing a general form of the absorber design equation the simplified linear relationship shown in Equation 4-3 will be used here.

The molar flux N_A has now been expressed in terms of an actual concentration of A in the bulk gas phase (PY_A), a concentration of A in equilibrium with the bulk liquid (PY_A^*), and the reciprocal of the two individual resistances to mass transfer. The quantity $\left(\frac{1}{k_g} + \frac{H}{k_\ell}\right)^{-1}$ is normally represented by the symbol K_g, the overall gas-phase mass transfer coefficient. Thus,

$$N_A = K_g P(Y_A - Y_A^*)(\text{mole/cm}^2\text{-sec}) \qquad (4\text{-}6)$$

Equation 4-5 or Equation 4-6 may be applied to a scrubber by writing a mass balance for component A across a differential element of scrubber volume. The amount of component A transferred from the gas phase per unit time is equal to the integral of the product of the molar flux N_A and the interfacial area for mass transfer. This "standard" design equation is given by

$$-\int \frac{dy}{(y-y^*)} = \int \frac{K_g aPdV}{G} \qquad (4\text{-}7)$$

In Equation 4-7, G is the molar gas flow rate in the scrubber, "a" is the amount of interfacial mass transfer area per unit of scrubber volume, and dV is a differential element of scrubber volume. If $y \gg y^*$, the left-hand side of Equation 4-7 can be simplified. For the conditions found during the pilot plant tests y was over 10^4 times larger than y*. Assuming G is constant over the entire absorber (this is valid when the species being sorbed is a minor

component) and taking an average value of $K_g a$, Equation 4-7 can be integrated to give Equation 4-8.

$$\ell n \left(\frac{Y_A \text{ in}}{Y_A \text{ out}} \right) = \frac{K_g aPV}{G} \tag{4-8}$$

If the SO_2 removal efficiency R is defined as

$$R = \frac{Y_{in} - Y_{out}}{Y_{in}} \tag{4-9}$$

then an expression relating the removal efficiency to a set of scrubber operating variables can be derived

$$R = 1 - \exp(-K_g aPV/G) \tag{4-10}$$

For a packed scrubber such as the one used for the pilot-scale tests the volume can be expressed by Equation 4-11.

$$V = DA_c \tag{4-11}$$

In Equation 4-11, D is the packing depth in the absorber and A_c is the cross-sectional area of the absorber. Substituting Equation 4-11 into Equation 4-10 the removal can now be expressed by Equation 4-12.

$$R = 1 - \exp(-K_g aPDA_c/G) \tag{4-12}$$

This expression which was developed based on absorption theory can now be used to correlate the data collected during the test program.

Correlation of Test Data--

By examining Equation 4-12 it can be seen that the following three major variables can impact the SO_2 removal rate in an absorber:

- The residence time of the flue gas, DA_c/G.
- The interfacial mass transfer area, a.
- The overall mass transfer coefficient, K_g.

The scrubber pressure is not a variable of practical significance since most scrubbers operate essentially at atmospheric pressure.

In designing an absorber it is important to be able to predict how a change in design parameters will impact operation of the absorber. The variables which can be changed to influence the flue gas residence time are packing depth, the cross-sectional area of the absorber and the gas flow rate. The impact on residence time of changing any of these variables is well defined by Equation 4-12 and will not be discussed further.

The remaining variables which can influence SO_2 removal are the overall mass transfer coefficient and the interfacial area for mass transfer. Unfortunately, the relationship between these variables and absorber design parameters is not well defined. In fact, the only practical way to quantify this relationship is to develop an empirical correlation. In order to develop a correlation between K_g, a, and scrubber operating parameters, it is necessary to examine the definition of the mass transfer coefficient and the interfacial area. This will identify which operating parameters influence Kg and a and thus provide a basis for correlating the experimental data developed during the test program.

The interfacial area for mass transfer is primarily a function of the contactor design although it may also be affected by both the gas and liquid phase flow rates. The extent to which the interfacial area will depend on these variables is determined by the scrubber design. For example, it would be expected that the "a" term would be less dependent on the liquid flow rate in a packed absorber than it would in a spray absorber. In a spray absorber, an increase in the liquid rate would generally create more droplets of a smaller average size, while in a packed absorber this same change would tend to alter the liquid throughput rate with only a minimal, if any, increase in

vapor/liquid mass transfer area. However, the gas rate would be expected to significantly affect the mass transfer area in a packed absorber. As discussed earlier, this agrees with the behavior observed during the pilot-scale tests.

The overall mass transfer coefficient, K_g, is influenced by a number of different process variables. To assess these effects, recall the definition of K_g:

$$K_g = \left(\frac{1}{k_g} + \frac{H}{k_\ell}\right)^{-1} \qquad (4\text{-}13)$$

The individual mass transfer coefficients k_g and k_ℓ basically describe the diffusion rate of a component across two hypothetical stagnant films which represent the interface between the gas and the scrubbing liquid. Thus, any process variable that changes the physical or chemical properties of these films may affect k_g or k_ℓ. Variables which change the turbulence in the gas and liquid boundary layers will affect the mass transfer coefficients k_g and k_ℓ. Such variables include gas and liquid flow rates and contactor type. In general, the variables which affect the mass transfer coefficients also tend to influence the interfacial area.

The other variables which can influence K_g are related to the chemistry of the MgO scrubbing process. The effects of system chemistry can be explained by considering the three mass transfer cases associated with the stagnant gas and liquid film model. These are 1) gas film limiting, 2) liquid film limiting, and 3) gas and liquid film resistances both contributing to an overall mass transfer limitation. Discussion of the first two cases is sufficient for purposes of unterstanding important variable effects since the third case is a combination of the two extremes.

Gas film limitation--The principal example where mass transfer could be gas film limited is in the case of low SO_2 inlet concentrations. At low inlet SO_2 concentrations and high L/G ratios, increases in the inlet SO_2

concentration can be experienced with no loss in scrubbing efficiency. This is the same behavior which was observed during the pilot-scale test program and it indicates that the liquid phase resistance becomes more significant as the flue gas SO_2 concentration increases.

It should be emphasized that the point at which a system changes from gas film limiting to liquid film limiting is determined by a number of factors including gas and liquid velocities as well as available liquid phase alkalinity. The gas and liquid velocities will influence both the interfacial area and the thickness of the gas and liquid boundary layers. These parameters in turn affect the transition from gas film to liquid film mass transfer limiting. The liquid phase alkalinity will also have a marked effect on mass transfer limitations.

Liquid film limitations--It follows from the above discussion that during the pilot-scale tests, the system was partially liquid film mass transfer limited. This limitation in turn is a strong function of the total liquid phase alkalinity. When SO_2 is sorbed from a flue gas by an aqueous scrubbing liquor, sulfurous acid is formed. The equilibrium reaction which controls the SO_2 sorption step, together with the first ionization reaction of sulfurous acid is shown in Equation 4-14.

$$SO_2\ (g) + H_2O \rightleftarrows H_2SO_3\ (aq) \rightleftarrows H^+ + HSO_3^- \qquad (4\text{-}14)$$

Any species which is basic with respect to the first sulfurous acid ionization reaction will cause this equilibrium to be shifted to the right and will increase the scrubbing liquor's SO_2 sorption capacity. In the system tested, the principal source of liquid phase alkalinity was $SO_3^=$ which is associated with the Mg^{++} ion. As discussed earlier, pH is a good measure of the $SO_3^=$ concentration in the MgO scrubbing system and, therefore, a good measure of the liquid phase alkalinity.

Another major source of alkalinity during the pilot-scale tests resulted from the dissolution of $MgSO_3 \cdot 6H_2O(s)$ in the absorber to form $SO_3^=$. The rate at which the solids dissolved can be expressed by Equation 4-15.

$$D = K_d A\,[1-RS] \qquad (4\text{-}15)$$

In Equation 4-15, D is the rate of solids dissolution, K_d is the dissolution rate constant, A is the surface area of $MgSO_3 \cdot 6H_2O$ solids in the absorber and RS is the relative saturation of $MgSO_3 \cdot 6H_2O$ in the absorber. Using Equation 4-15 and integrating over the conditions found in the absorber, the amount of $MgSO_3 \cdot 6H_2O(s)$ which dissolves can be calculated.

The principal factors which affect the dissolution rate are the driving force and the solids surface area. In order to account for the contribution of solids dissolution to liquid phase alkalinity, the absorber operating parameters which influence the dissolution rate must be considered.

The driving force for dissolution of solids is based on the relative saturation of $MgSO_3 \cdot 6H_2O(s)$ which, in the MgO scrubbing system, is a strong function of pH. As the pH is reduced, the concentration of $SO_3^=$ is reduced and the relative saturation of $MgSO_3 \cdot 6H_2O(s)$ drops below 1 thus creating a driving force for solids dissolution. Therefore, the pH is a good measure of the driving force for dissolution. However, it should be emphasized that the pH within the absorber depends not only on the pH of the absorber feed, but also on the quantity of SO_2 absorbed per unit volume of slurry fed to the absorber. As discussed earlier, "SO_2 pickup" is dependent on inlet SO_2 concentration, gas flow rate, liquid flow rate, and gas residence time.

The surface area of solids in the absorber depends on two factors. The first is the size of solid particles and the second is the number of particles present. For the pilot-scale tests, the surface area of the particles can be approximated by Equation 4-16.

$$A = C \cdot W \cdot L \qquad (4\text{-}16)$$

where C is a constant, W is the weight percent solids in the scrubbing slurry and L is the slurry feed rate. This assumes a relatively constant size distribution of particles throughout the test program.

In summary, it appears that there are several key operating parameters which can affect the overall mass transfer coefficient and the interfacial mass transfer area. These operating parameters include liquid and gas flow rates or velocities, inlet SO_2 concentration, the pH of the absorber feed, and the weight percent of $MgSO_3 \cdot 6H_2O$ solids in the absorber feed. As evident from the preceding discussion, several of these variables can influence K_g or a in a complex manner. For example, pH influences liquid phase alkalinity and the rate of solids dissolution in the scrubber. Therefore, it is very difficult to define how each variable can influence the product, $K_g a$.

Design Equation Development--

Because of the difficulty in defining the precise relationship between $K_g a$ and the absorber operating parameters, an empirical approach was taken. This approach involved selecting a form for the relationship between $K_g a$ and the key absorber operating parameters. The form selected is shown in Equation 4-17.

$$K_g a = b_0 \cdot \left(\frac{L}{A_c}\right)^{b_1} \cdot \left(\frac{G}{A_c}\right)^{b_2} \cdot (pH)^{b_3} \cdot (W)^{b_4} \cdot (SO_2)^{b_5} \qquad (4\text{-}17)$$

where $\frac{L}{A_c}$ = slurry velocity in the absorber ($\ell/sec \cdot m^2$)

$\frac{G}{A_c}$ = gas velocity in the absorber ($Nm^3/hr \cdot m^2$)

pH = pH of absorber feed slurry

W = weight percent $MgSO_3$ solids in the absorber feed

SO_2 = SO_2 concentration of inlet gas (ppm)

and b_0 through b_5 are empirical constants which must be determined based on experimental data. It should be noted that gas and liquid velocities are

used in Equation 4-17 as opposed to flow rates. In cases where the absorber design is fixed, these terms can be used interchangeably since velocities are directly proportional to flow rates. However, when developing a general equation which will be used to scale up an absorber design, the gas and liquid velocities are the correct form of the variables since it is velocity, and not flow rate, which influences $K_g a$. The empirical constants in Equation 4-17 were determined using linear least squares regression applied to the data developed during the pilot-scale tests. In order to apply this technique, it was necessary to transform Equation 4-17 to a linear combination of the absorber operating parameters. Taking the logarithm of both sides of Equation 4-17 yields:

$$\ell n\ K_g a = \ell n\ b_0 + b_1 \ell n\ (L/A_c) + b_2 \ell n\ (G/A_c) + b_3 \ell n\ (pH) + b_4 \ell n\ (W) + b_5 \ell n\ (SO_2) \qquad (4\text{-}18)$$

Least squares regression analysis was used to determine b_0 through b_5 in equation 4-18, using the data from the tests as given in Appendix C. The coefficients were found to have the following values:

$b_0 = 4.36 \cdot 10^{-3}$
$b_1 = 0.899$
$b_2 = 1.00$
$b_3 = 2.86$
$b_4 = 0.284$
$b_5 = -0.621$

Including these values in Equation 4-17 and substituting for $K_g a$ in Equation 4-12, SO_2 removal as a function of absorber operating parameters is quantified by Equation 4-19, where R is the fractional efficiency for SO_2 removal.

$$R = 1 - \exp\left[(-4.36 \cdot 10^{-3}) \left(\frac{L}{A_c}\right)^{0.899} (pH)^{2.86} (W)^{0.284} (SO_2)^{-0.621} (P)(D)\right] \qquad (4\text{-}19)$$

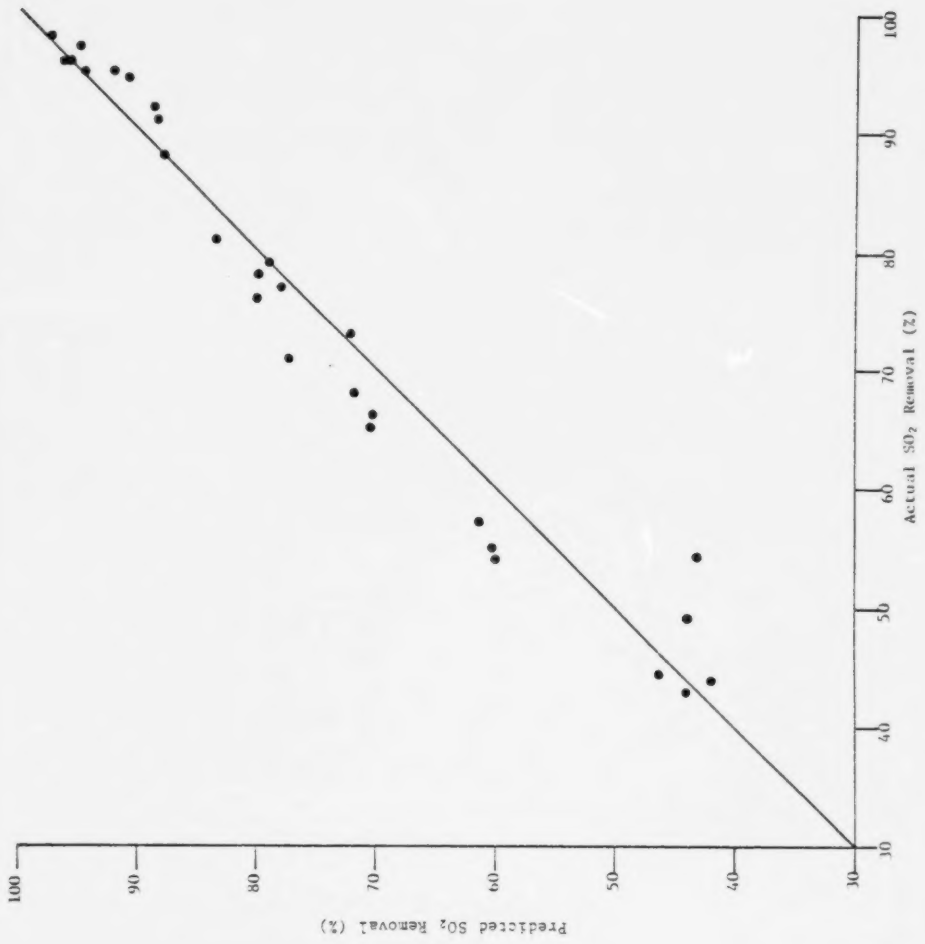

Figure 4-2. Ability of design equation to predict SO_2 removal efficiency.

The units for use in Equation 4-19 are as follows: L-ℓ/sec, SO_2-ppm, P-atm, D-cm, A_c-m^2. It is interesting to note that in Equation 4-19, the flue gas flow rate does not appear. This is due to the offsetting effect discussed earlier. By increasing the gas rate, more SO_2 enters the absorber and thus tends to lower the removal. However, increasing the gas flow rate also increases the value of $K_g a$ (Equation 4-17) and thus offsets the effect of additional SO_2 entering the absorber. The reader is cautioned that this is only true over the range of gas velocities tested during the program.

Figure 4-2 illustrates the ability of Equation 4-19 to predict SO_2 removal as a function of absorber operating parameters. As shown, the correlation between actual and predicted removal is quite good with a correlation coefficient of 0.98.

Figures 4-3, 4-4, and 4-5 give a further indication of how well Equation 4-19 predicts actual test results. These figures show predicted removal as a function of L/G, pH, and SO_2 concentration respectively. In addition, actual test data points are shown in the figures. The data points presented represent tests conducted to quantify the relationship between SO_2 removal efficiency and the scrubber operating parameters. As shown, Equation 4-19 closely approximates the actual behavior observed during the test program.

Design Equation Evaluation--

By examining Equation 4-19, the impact of absorber operating parameters on SO_2 removal can be assessed. The value of the exponents in Equation 4-19 are a measure of the significance of each parameter's impact on SO_2 removal efficiency. In other words, the larger the exponent, the more significant the effect of the variable on SO_2 removal. In general, the absorber operating parameters can be divided into two groups in terms of impact on removal efficiency; major and minor. The major parameters (based on the exponent values in Equation 4-19) are liquid flow rate, pH, and packing depth. Minor parameters are SO_2 concentration and weight percent solids. The relative influence of each parameter is illustrated in Figure 4-6 in which each parameter is varied from a base level while the other parameters are held constant.

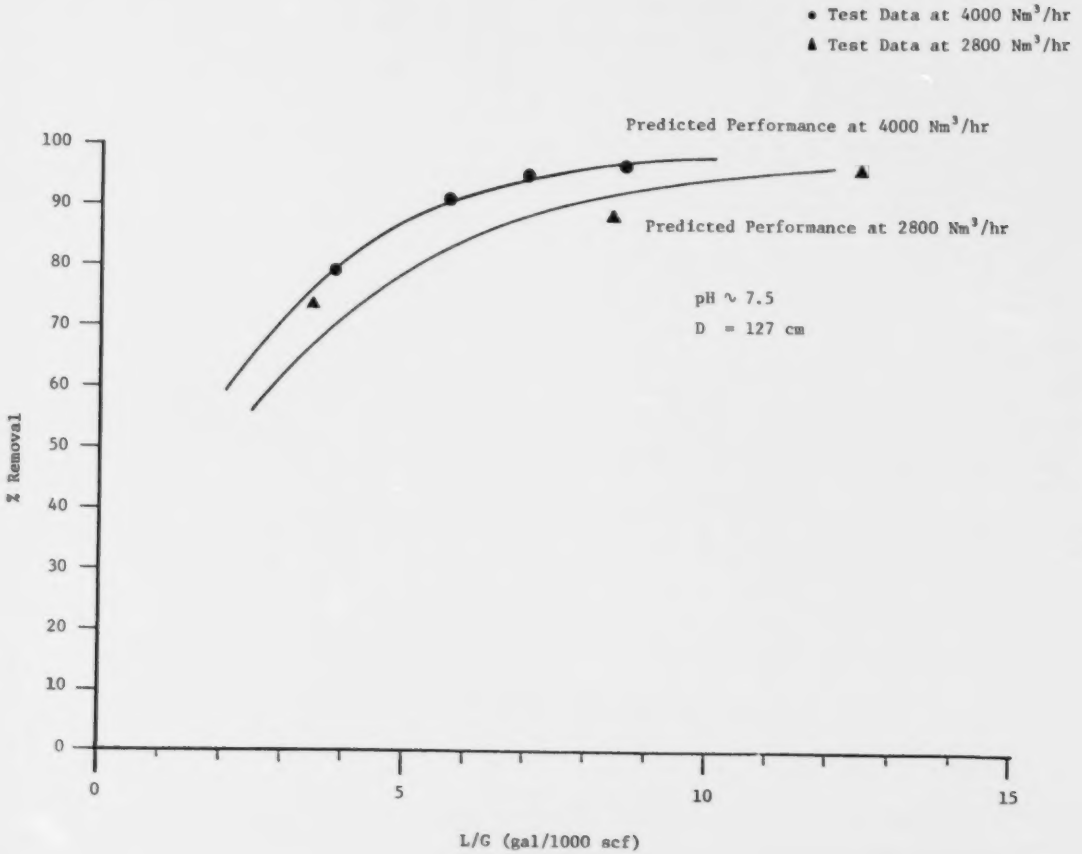

Figure 4-3. Agreement of predicted and selected experimental values for SO_2 removal as a function of L/G ratio.

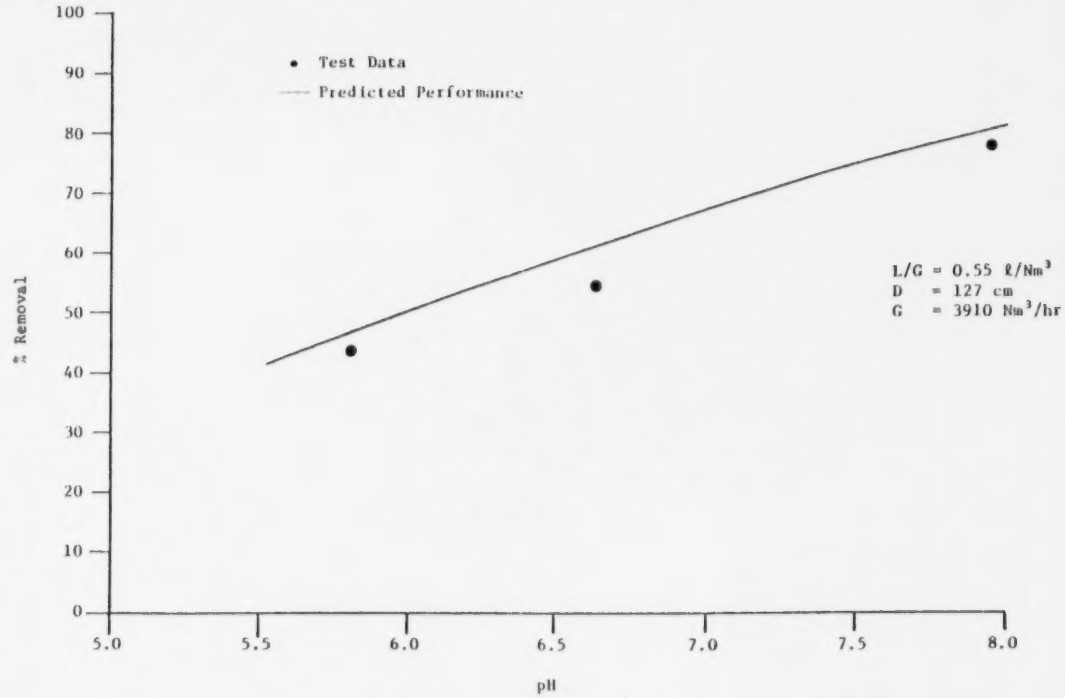

Figure 4-4. Agreement of predicted and selected experimental values for SO_2 removal as a function of absorber feed pH.

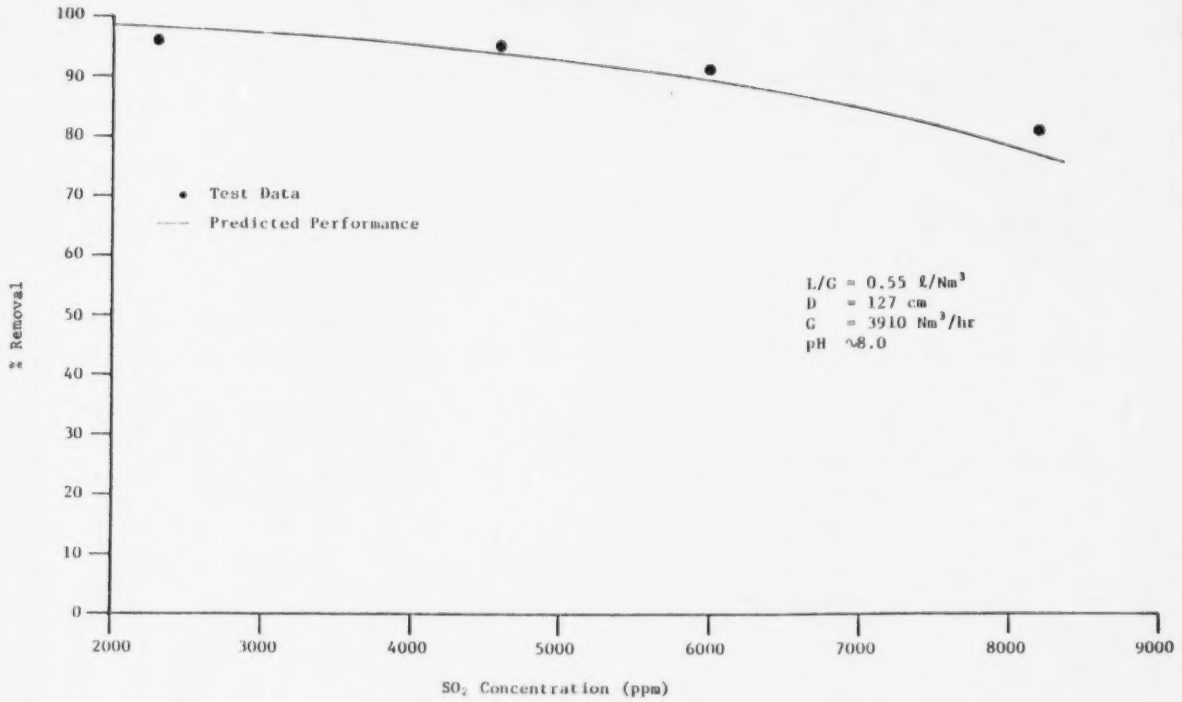

Figure 4-5. Agreement of predicted and selected experimental values for SO_2 removal as a function of inlet SO_2 concentration.

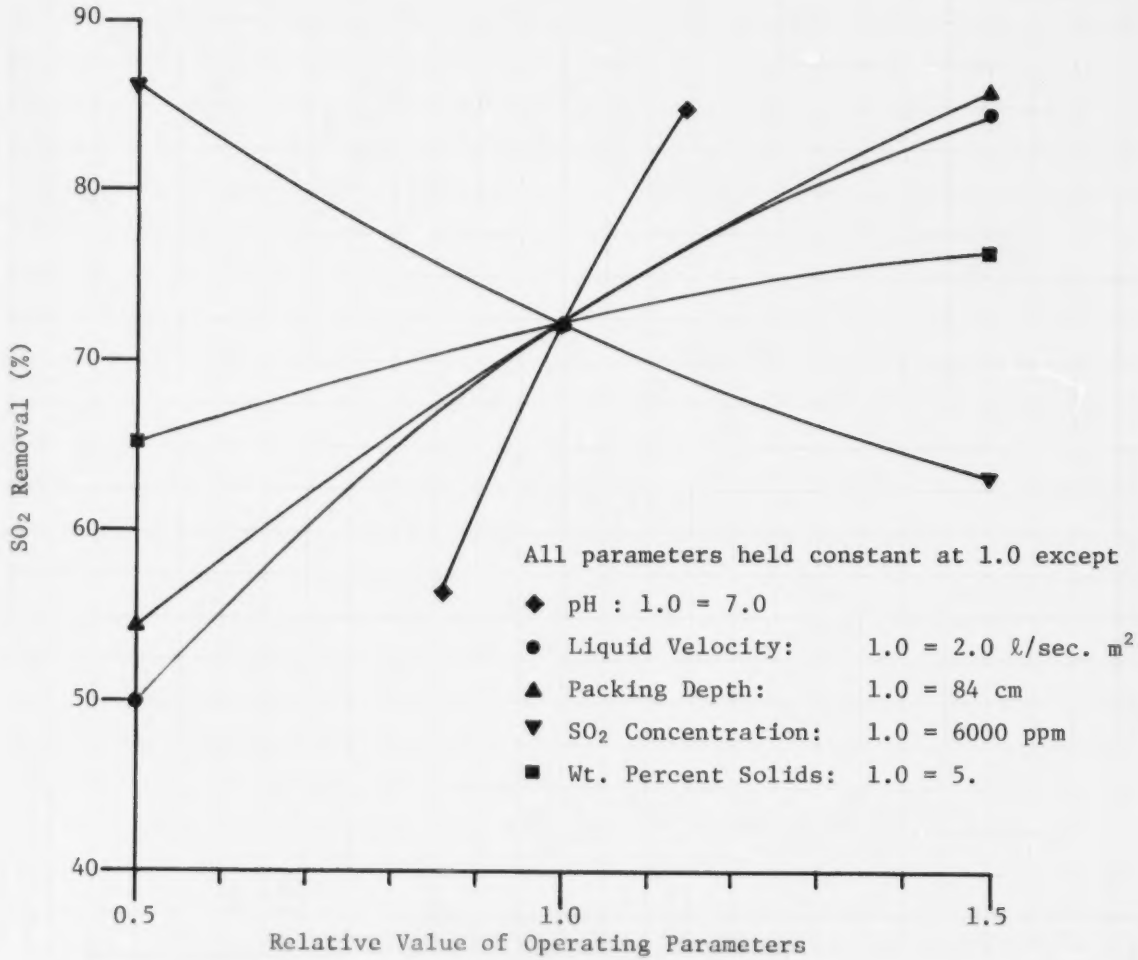

Figure 4-6. Relative influence of absorber operating parameters on SO_2 removal efficiencies.

As shown, pH is the most significant variable with liquid rate and packing depth having about equal but a less significant influence on removal efficiency.

It should be noted that interpretation of Figure 4-5 requires consideration of more than the relative influence of absorber operating parameters. The effect and difficulty of changing the operating parameters must also be examined. For example, a 50 percent increase in either slurry feed rate or packing depth produces about an equal increase in the predicted SO_2 removal efficiency, but the effect of these changes on absorber pressure drop is significantly different. By increasing the packing depth 50 percent, the pressure drop should also increase 50 percent while an increase in the slurry feed rate should not significantly increase absorber pressure drop. Again, it is important that this and other trade-offs be considered in interpreting Equation 4-19.

Design Equation Applicability--

Equation 4-19 represents an absorber design equation which can be used to predict the performance of a particular absorber design configuration. However, this equation is only valid for specific conditions and ranges of absorber operating parameters. The following discussion identifies the major restrictions which must be observed in applying Equation 4-19 to a particular situation.

The most obvious restriction on Equation 4-19 is that it is only applicable for use with a MgO scrubbing system processing gas in an absorber packed with 2.5 cm (1 inch) tellerette packing. This design equation is not applicable to other absorber configurations (*e.g.*, a spray tower) or other types of packing material. The other principal restriction for use of Equation 4-19 is that the scrubber operating parameters selected for an absorber design must be within the range in which the parameters were tested during the program. Specific ranges for these parameters are presented in Table 4-3. The applicable range for each parameter represents the range over which the parameters were varied during the test program. However, in some cases there are

design considerations which limit the ranges presented in Table 4-3. The following discussion examines each parameter and identifies the design principles which must be considered in selecting levels for the absorber operating parameters.

TABLE 4-3. RANGE OF ABSORBER OPERATING PARAMETERS APPLICABLE TO DESIGN EQUATION

Operating Parameter	Applicable Range
Gas Velocity (m/sec)	1.8 to 2.6
pH	6.0 to 8.0
Liquid Velocity (ℓ/sec$\cdot$m^2)	1.0 to 5.4
Weight Percent Solids	4 to 10
SO_2 Concentration (ppm)	2000 to 9000

Gas velocity--Although gas velocity does not appear in the design equation, it is an important design consideration. As discussed earlier, operation of the absorber outside the applicable range of gas velocities can result in changes in removal which are not accounted for by the design equation. In addition, at gas velocities above 2.6 m/sec, pressure drop in the absorber increases rapidly and at some gas velocity flooding of the absorber will occur.

The relationship between gas velocity and absorber pressure drop is illustrated in Figure 4-7. As shown, only a small increase in gas velocity above 2.6 m/sec results in a large increase in absorber pressure drop. It should be noted that the data in Figure 4-7 are based on slurry feed rates in the range shown in Table 4-3. Operation at a liquid rate outside this range may produce a somewhat different absorber pressure drop.

In examining Figure 4-7, it appears that good absorber design practice would not specify a gas velocity above 2.6 m/sec because of the significant increase in pressure drop. In designing an absorber, the gas velocity would be selected based on a trade-off of absorber cross-section vs. pressure drop.

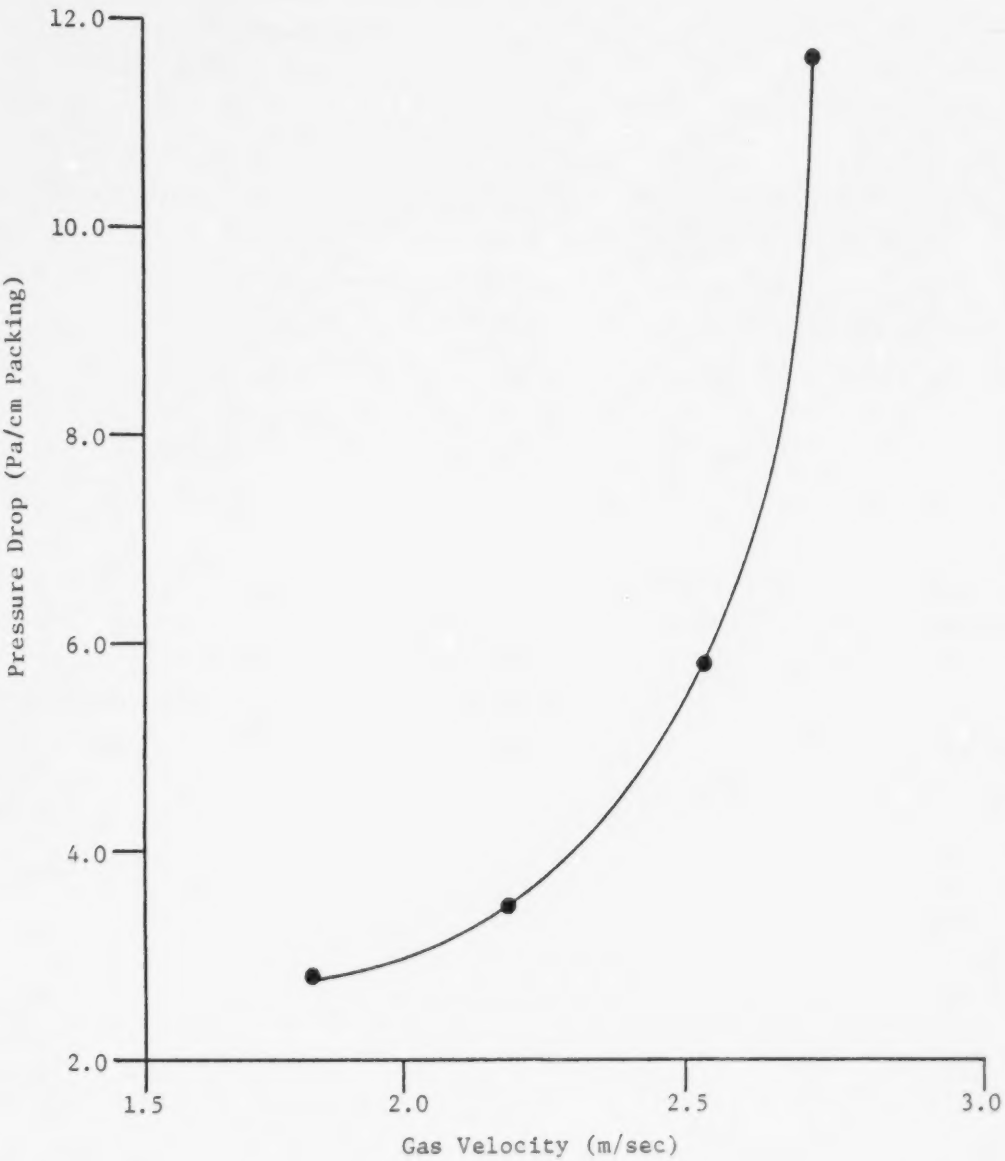

Figure 4-7. Absorber pressure drop as a function of gas velocity.

Relatively low gas velocities result in a larger absorber with a lower pressure drop while high gas velocities result in a smaller absorber with a higher pressure drop. The trade-off which must be evaluated is an economic one; the capital costs for a larger absorber vs. the operating costs of overcoming a higher pressure drop. Figure 4-7 can be used as a basis for evaluating this trade-off.

pH--The pH of the absorber feed slurry is one of the most significant operating parameters tested. However, the range of pH values tested was limited to between 6 and 8. The principal reason for this limitation is based on the equilibrium shift between HSO_3^- and $SO_3^=$. At pH 6, the aqueous phase sulfite is nearly all HSO_3^- while at pH 8 it is nearly all $SO_3^=$. Since $SO_3^=$ is the principal species which is alkaline with respect to SO_2 sorption, increasing the pH above 8 should not produce a significant increase in removal efficiency. Further, at pH levels above 8.0 in the absorber feed, the potential for formation of $MgSO_3 \cdot 6H_2O(s)$ solid scale in the absorber is increased. At pH levels below 6.0 there is essentially no $SO_3^=$ present and removal efficiency would be expected to continue to decline.

In selecting a pH for absorber operation it appears that the highest practical pH level should be chosen. Based on the pilot-scale test results it appears that this level is between 7.5 and 8.0. At pH 8, very little $Mg(OH)_2$ solids were found in the scrubber feed slurry and, as a result, no scale formation was observed in the absorber. Therefore, it appears that there is no significant cost associated with operating at pH 8 vs. pH 6, while a significant improvement in SO_2 removal efficiency would result.

Liquid velocity--The liquid velocity or slurry feed rate is an important design variable which must be specified to use the absorber design equation. The range of liquid velocities presented in Table 4-3 are based principally on the range of feed rates examined during the test program. However, the upper end of this range is limited by practical considerations. The test results showed (Figure 4-3) that the effects of increasing the liquid velocity diminish until a limiting value for removal efficiency is finally reached.

The liquid velocity at which this occurs depends on the other absorber operating parameters, principally pH and packing depth. As discussed above, the optimum pH is about 8.0 so this can essentially be considered constant. As a result, the limiting liquid velocity will be a strong function of the packing depth.

The relationship between liquid velocity, packing depth and SO_2 removal is illustrated in Figure 4-8. As shown, a trade-off exists between liquid rate and packing depth. This trade-off must be evaluated in terms of the costs of increased pumping requirements vs. the costs for additional packing and the associated increase in pressure drop.

The effect of liquid velocity on absorber pressure drop is very small in the range of gas flow rates tested. As a result the impact of liquid velocity on absorber pressure drop is not a significant design consideration. For liquid velocities above 5.4 $\ell/sec \cdot m^2$, absorber pressure drops may be somewhat higher than those shown in Figure 4-7.

Weight percent solids--The weight percent of $MgSO_3 \cdot 6H_2O$ solids is another absorber operating parameter which must be included in the design equation. However, the impact of the weight percent solids level on removal efficiency is relatively minor (Figure 4-6). In an MgO scrubbing system, the quantity of solids in the circulation slurry will be a function of the system design, primarily the solids separation equipment. In designing an MgO system, first consideration should be given to the ability of process equipment to handle solids rather than to the impact of solids on absorber performance. As a general guideline based on the pilot-scale tests, 10 weight percent appears to be a workable slurry in terms of pumpability and the ability of the absorber to operate without plugging.

SO_2 concentration--The design equation developed from the pilot-scale test results is only applicable for SO_2 concentrations up to 9000 ppm. For applications at SO_2 concentrations above 9000 ppm, a conservative approach

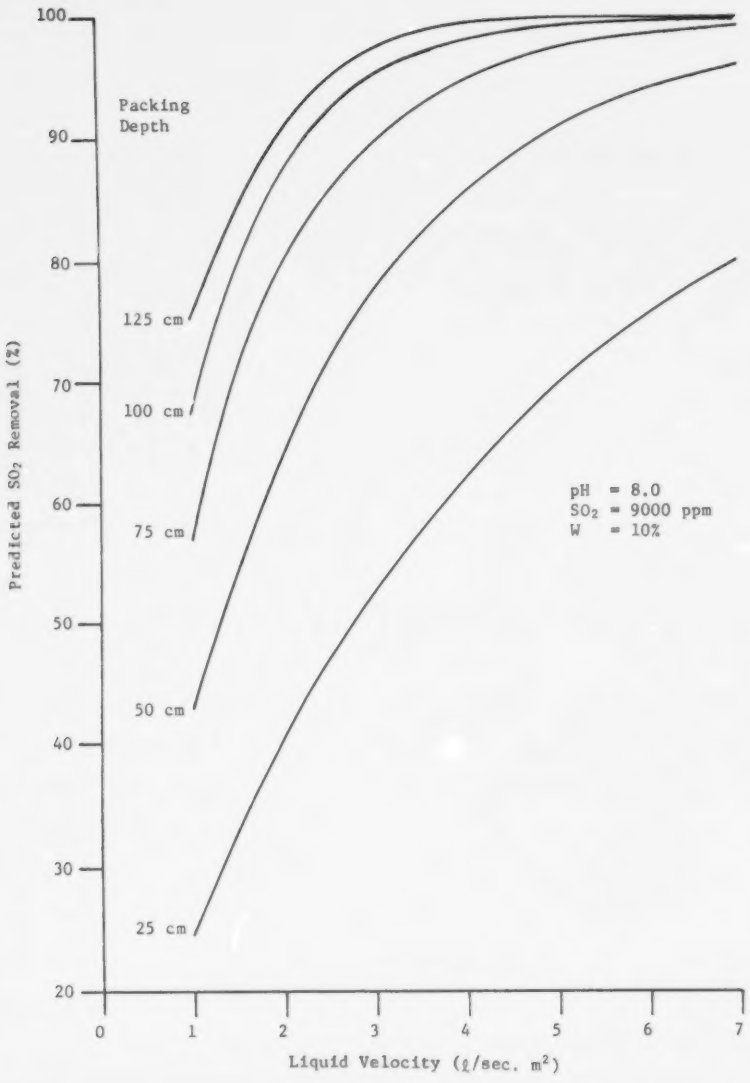

Figure 4-8. The effect of liquid velocity and packing depth on predicted SO_2 removal.

should be taken since removal may drop off more rapidly than Equation 4-19 predicts. In fact, bench- or pilot-scale tests may be necessary for applications to gas streams with SO_2 concentrations above 9000 ppm.

SO_2 concentration is not usually a design variable. Rather, it is a characteristic of the off-gas stream to be treated. As such, it must be considered in evaluating absorber performance, but it is not usually controllable to improve performance. However, in cases where some measure of control can be imposed on off-gas SO_2 concentration by dilution or prevention of dilution, processing a more concentrated gas stream would result in a smaller absorber. This is illustrated in Figure 4-9 along with the predicted change in slurry feed rate to the absorber. As shown, if the SO_2 concentration decreases due to dilution, the absorber cross-section must increase to maintain constant gas velocity. At the same time the liquid velocity required to maintain constant SO_2 removal decreases. However, the liquid flow rate actually increases with decreasing SO_2 concentration. This is due to the fact that the increase in the cross-sectional area of the absorber is proportionally greater than the decrease in liquid velocity due to lower inlet SO_2 concentrations as shown in the design equation.

Examination of Figure 4-9 clearly indicates the benefits of processing a more concentrated SO_2 stream. This should be considered in cases where it is possible to exercise some control over the SO_2 concentration of the gas stream being processed.

Packing depth--The quantity of packing material in an absorber is an important design consideration in terms of both SO_2 removal and absorber pressure drop. As the packing depth increases, SO_2 removal will also increase at an exponentially decreasing rate while pressure drop increases proportionally. This behavior is illustrated in Figure 4-10. As shown, increasing packing depth from 10 to 50 cm produces a relatively rapid increase in removal. Increasing packing depth above 50 cm produces less and less of an increase in SO_2 removal efficiency while the pressure drop is proportional to the packing depth for all packing depths.

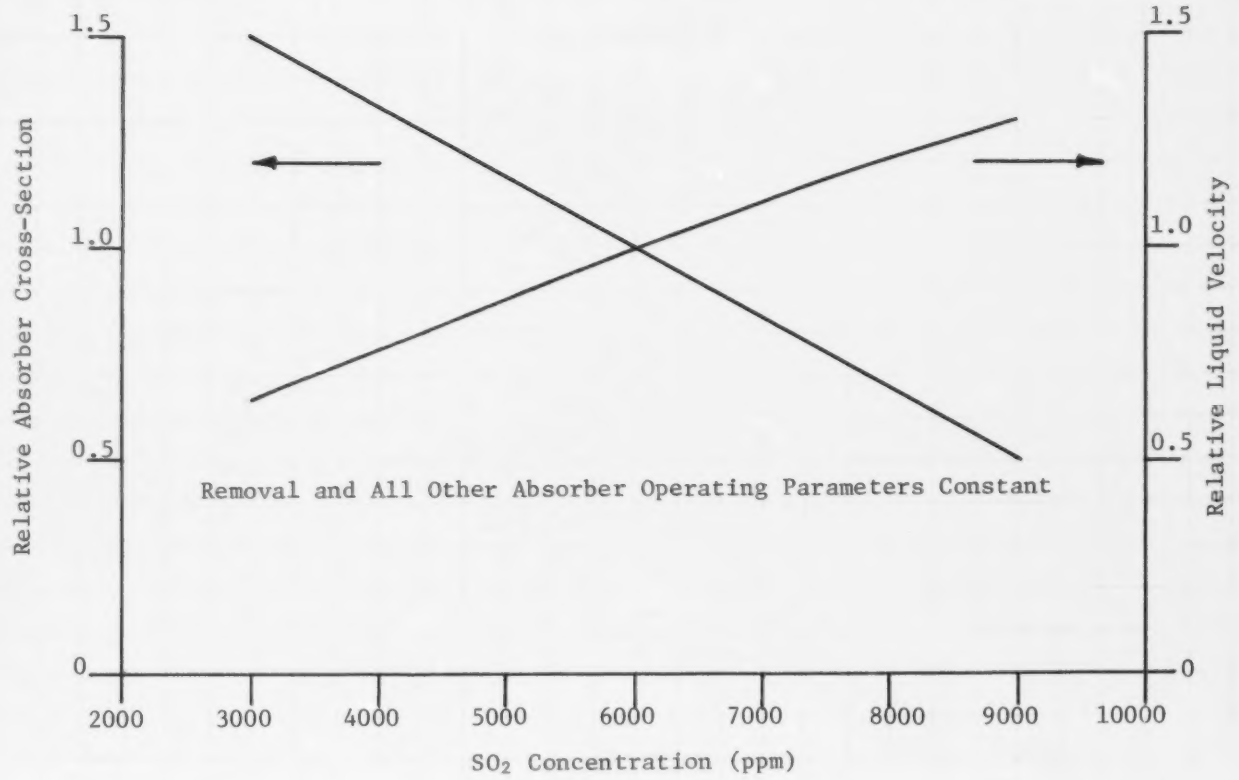

Figure 4-9. Relative absorber cross-section and liquid velocity as a function of SO_2 concentration changes due to dilution/concentration.

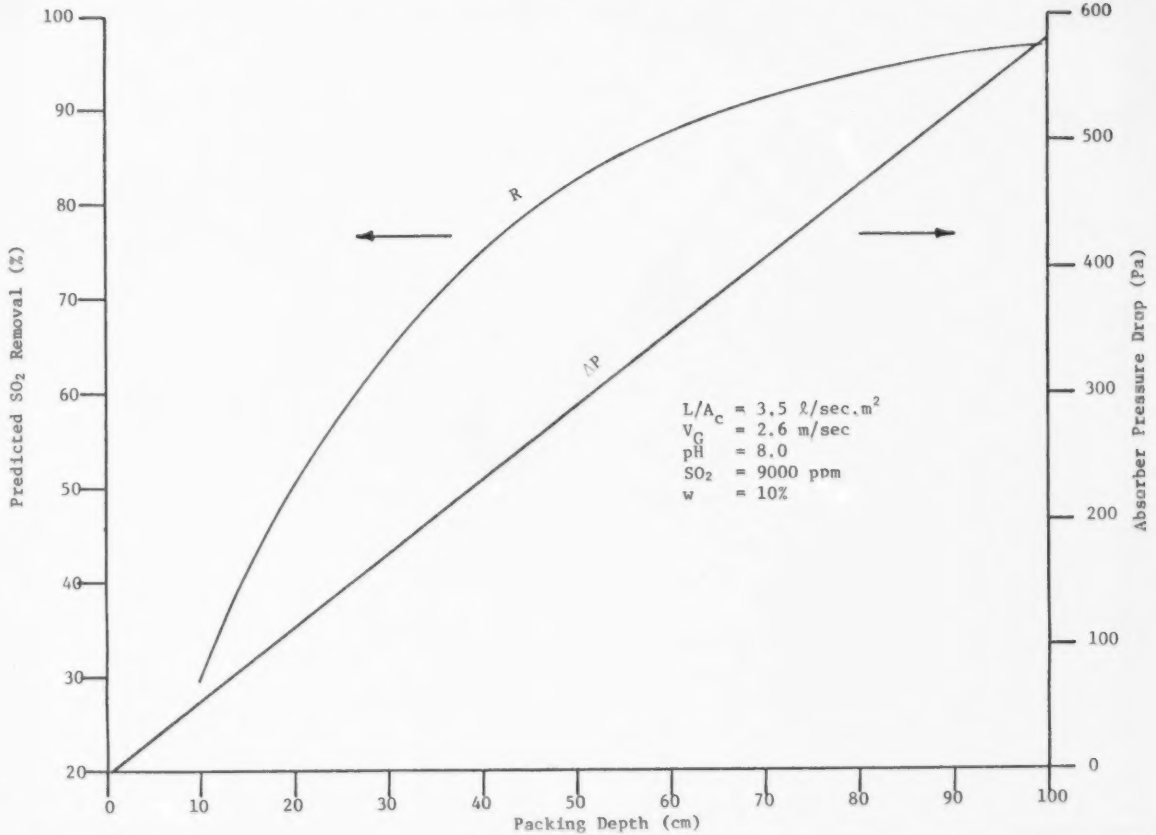

Figure 4-10. Absorber pressure drop and SO_2 removal as a function of packing depth.

It should be noted that Figure 4-10 is valid for one set of absorber operating parameters. Changes in liquid velocity, gas velocity, or other parameters can shift the curve in Figure 4-10 to the right or left. In selecting a packing depth for an absorber design, the complex interactions between the absorber operating/design parameters must be subjected to an economic evaluation to determine the optimum level for each parameter. Since this type of evaluation requires specific cost data, it is beyond the scope of this study.

Summary--Each of the absorber operating parameters can impact the removal efficiency predicted by Equation 4-19. In using this equation to design an absorber, the range in which the equation is applicable must be considered. Also, other design considerations such as process equipment restrictions on weight percent solids and the trade-off between absorber cross-section and pressure drop must be evaluated.

4.2 DURATION TEST RESULTS

The results of the short-term variable tests described in Section 4.1 are useful for characterizing absorber performance as a function of certain operating parameters. However, there are several issues which could not be addressed during the short-term tests. These issues are:

- the rate or fraction of $SO_3^=$ oxidized in the absorber,
- the stoichiometry of the absorber operation (*i.e.*, the number of moles of $Mg(OH)_2$ fed per mole of SO_2 removed from the gas), and
- closure of an overall material balance for the absorber system.

In order to address these issues, a duration test was conducted. This test was scheduled to operate at constant conditions for approximately 100 hours or until the level of all operating parameters and dependent variables had stabilized for 24 hours. Previous experience has shown that a test of this duration is sufficient to permit closure of an overall material balance within 10 percent.

Operating conditions for the duration test were selected based on the results of the short-term variable tests. This was done to try and "optimize" absorber operation for the duration test and to assure an SO_2 removal efficiency of over 90 percent. Planned and actual conditions for the duration test are presented in Table 4-4. As shown the actual conditions correspond closely to the planned conditions. The range shown for the actual test conditions is due in part to small fluctuations in system operation. However, the major reason for the range of actual conditions is due to a change in operation of the absorber after about 18 hours. This is illustrated in Figure 4-11 where a reduction in the liquid rate resulted in a corresponding decrease in SO_2 removal efficiency.

TABLE 4-4. PLANNED AND ACTUAL TEST CONDITIONS FOR DURATION TEST

Parameter	Planned level	Actual level
Gas Flow Rate	4000 Nm^3/hr	3940 Nm^3/hr
L/G ratio	1.13 (ℓ/Nm^3)	0.86-1.11 (ℓ/Nm^3)
pH	7.5	7.6-8.0
Packing Depth	127 cm	127 cm
Weight Percent Solids	8	6-14
SO_2 Removal	95%	90-99%

The change in absorber operating conditions was made because the absorber pressure drop began increasing beyond the levels observed during the short-term tests. The increase in absorber pressure drop was gradual at first, but they became relatively rapid as shown in Figure 4-12. Once the pressure drop reached 2 kPa the system was shut down. A visual inspection of the packed beds revealed a buildup of solids on the beds.

Initially, the solids buildup was attributed to a high level (12 wt%) of solids in the scrubber feed. Consequently, system operation was adjusted to increase the rate at which solids were removed from the process. After removing deposits from the absorber, the duration test was resumed but the problem

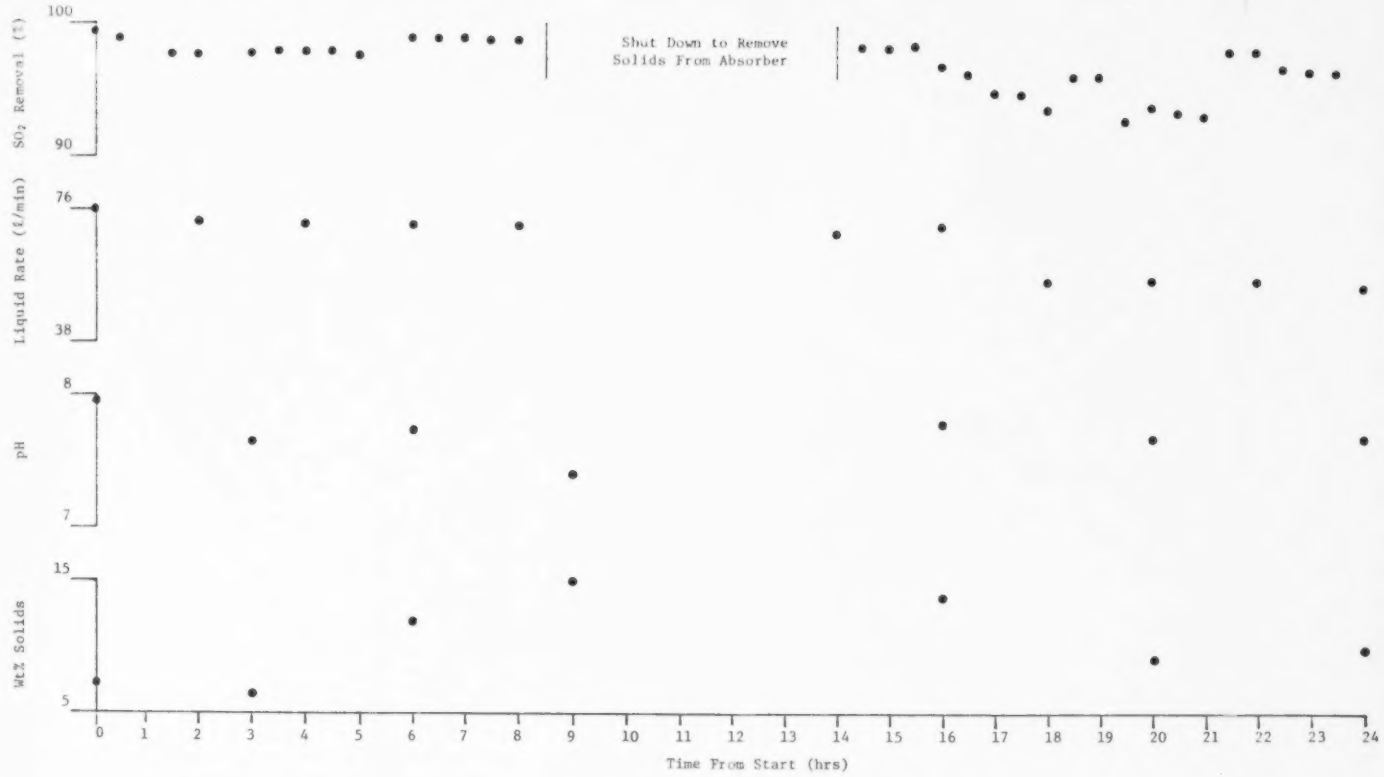

Figure 4-11. Operating parameter levels during duration test.

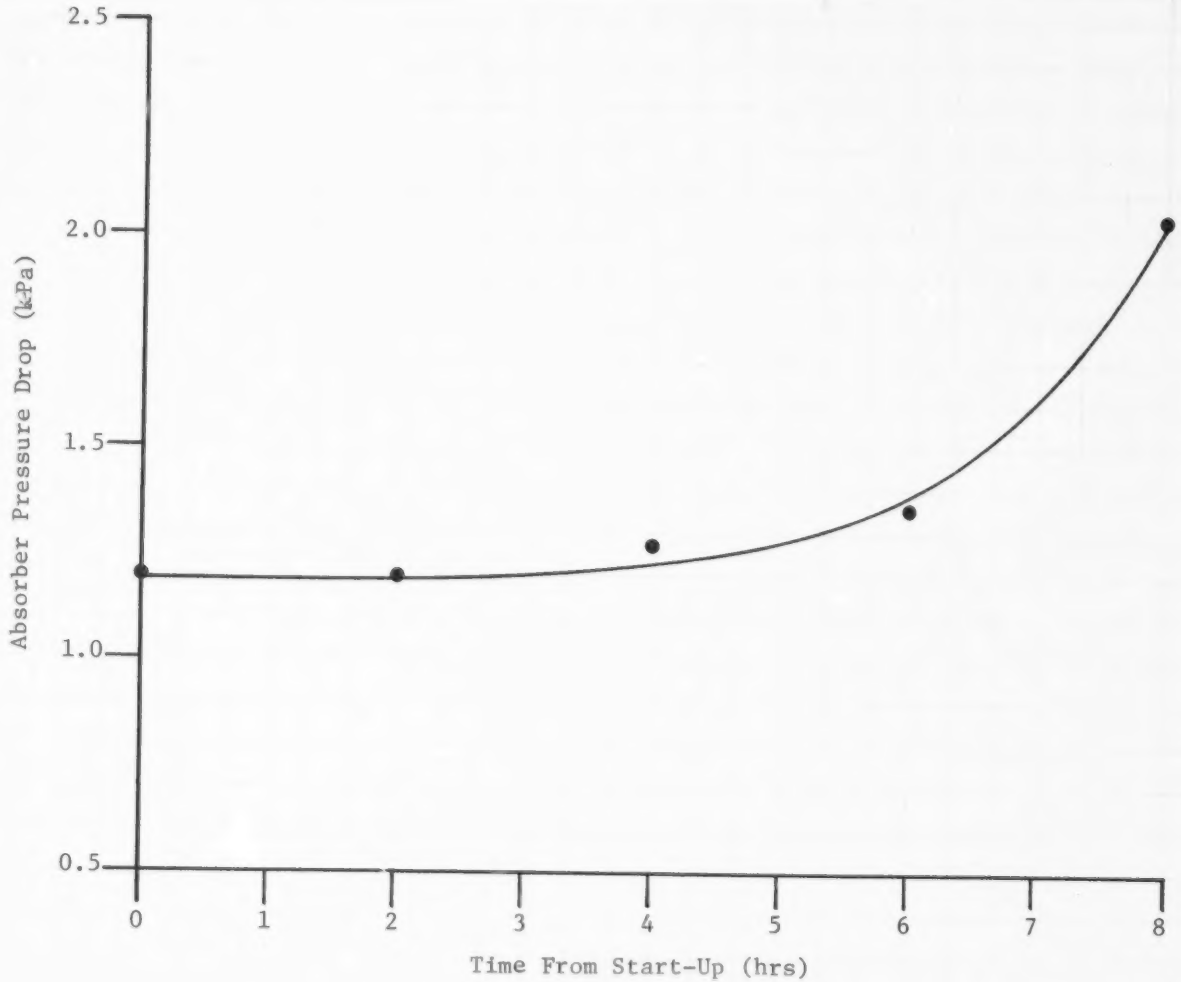

Figure 4-12. Absorber pressure drop during duration test.

was not solved and the absorber pressure drop began to increase again. During this period, SO_2 removal had been maintained at an unusually high level (over 97 percent). A decision was made to reduce the SO_2 removal to approximately 90 percent by reducing the liquid feed rate to the absorber.

Following the reduction in the liquid feed rate, no further increase in absorber pressure drop was observed. In fact, a decrease in pressure drop occurred. Unfortunately, the duration test was terminated about 6 hours after the liquid rate was reduced due to failure of the pilot system blower. Consequently, the steady-state absorber pressure drop could not be determined.

The variation in absorber pressure drop appears to be related to the SO_2 concentration at the scrubber outlet. At low (<100 ppm) outlet SO_2 concentrations, there is a reduced driving force for SO_2 absorption at the top of the packing bed and, therefore, little or no driving force for dissolution of $MgSO_3 \cdot 6H_2O$ solids. As a result, the solids tend to build up and plug the upper end of the packed bed. However, at higher (>500 ppm) outlet SO_2 concentrations, the driving force for SO_2 absorption and solids dissolution is correspondingly higher. This increased "acidity" at the upper end of the packed bed prevents solids from accumulating.

The relationship between outlet SO_2 concentration and plugging of the packed bed is a significant finding. This indicates that the removal which can be achieved using a packed absorber must be limited such that the SO_2 concentration at the absorber outlet is 500 ppm or higher. Of course, it is possible to achieve higher removals by placing a spray tower absorber downstream of the packed tower or it may be possible to remove SO_2 above the packed bed using a clear liquor spray. One method of accomplishing this in a full-scale system would be to route liquor which is normally returned from the centrifuge to the reaction tank to spray nozzles located above the packing bed. This would result in additional SO_2 removal while maintaining a sufficiently high SO_2 concentration at the outlet of the packed bed.

As mentioned earlier, the duration test was terminated due to a failure of the blower for the pilot system. This failure occurred after about 24 hours of operation and was due to erosion of phenolic resin from the blower wheel followed by acid corrosion of the wheel material. As a result of the wheel failure, the duration run and the test program were terminated. Consequently, the issues to be addressed by the duration test could not be resolved with the accuracy hoped for. The following discussion examines the 24 hour duration test data and each of the key issues. The discussion includes presentation of reduced data from the duration test and examination of possible sources of error.

4.2.1 Determination of Sulfite Oxidation in the Absorber

One important design variable in an MgO scrubbing system is the fraction of sorbed $SO_3^=$ which is oxidized to $SO_4^=$ in the absorber. This oxidation rate is important in terms of calciner operation since $MgSO_4$ is not as easily regenerated as $MgSO_3$. It is necessary to add a carbon source to the calciner in order to produce a reducing atmosphere which will permit $MgSO_4$ to be regenerated as shown in Equations 4-20 and 4-21.

$$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g) \qquad (4\text{-}20)$$

$$CO(g) + MgSO_4(s) \rightarrow CO_2 + MgO + SO_2 \qquad (4\text{-}21)$$

Because the addition of carbon to the calciner is proportional to the quantity of $MgSO_4$ present, it is desirable to quantify the $MgSO_4$ production rate. In addition, there was concern that the oxidation rate might be extremely high due to the unusually high oxygen concentration (19 percent) of the off-gas. Therefore, determination of the $SO_3^=$ oxidation rate was one of the principal objectives of the duration test.

A simple material balance is all that is needed to quantify $SO_3^=$ oxidation in the absorber. This material balance is represented by Equation 4-22.

$$\text{Oxidation} = V_S([SO_4^{=}]_F - [SO_4^{=}]_I) + V_B[SO_4^{=}]_B \quad (4\text{-}22)$$

In Equation 4-22, V_S and V_B are the liquid volumes of the absorber system (*i.e.*, reaction tank, clarifier, and clarifier overflow tank) and the volume of the bleed stream respectively. The liquid phase sulfate concentrations are:

- $[SO_4^{=}]_F$ = Final absorber system concentration
- $[SO_4^{=}]_I$ = Initial absorber system concentration
- $[SO_4^{=}]_B$ = Average concentration of the bleed stream

Only liquid phase sulfate concentrations are used in the calculation since there were no sulfates in the solid phase. An assumption which is implicit in Equation 4-22 is that no SO_3 is removed in the absorber. The impact of this assumption on estimated $SO_3^{=}$ oxidation will be discussed later in this section.

When the duration test was interrupted to remove solids from the absorber, a large quantity of slurry was also removed from the system. Because no attempt was made to quantify this discharge, it is not possible to use the initial operating period of the test to quantify sulfite oxidation. The oxidation calculations presented here are based on the final 8 hours of system operation. Table 4-5 shows the data used to compute the sulfite oxidation

TABLE 4-5. DATA REQUIRED TO CALCULATE SULFITE OXIDATION RATE

Parameter	Level
V_S	5830 ℓ
$[SO_4^{=}]_F$	.137 gmol/ℓ
$[SO_4^{=}]_I$	.175 gmol/ℓ
V_B	5870 ℓ
$[SO_4^{=}]_B$	.149 gmol/ℓ

Applying Equation 4-22 to the data in Table 4-5, the quantity of sulfate produced during the final 8 hours of the duration test can be computed

$$[SO_4^{=}]_p = 5830\ell\ [.137\ \text{gmol}/\ell - .175\ \text{gmol}/\ell] + 5870\ell\ [.149\ \text{gmol}/\ell]$$

$$= 653\ \text{gmol}$$

where $[SO_4]_p$ is the quantity of sulfate produced during the period. Now, during the same 8 hour period, 9900 gmols of SO_2 were removed from the flue gas. Taking the ratio of sulfate produced to SO_2 removed gives an oxidation fraction of 6.6 percent. The oxidation rate which can be computed by considering the time period and quantity produced is 1.36 gmol/min.

As shown in Table 4-5, the final sulfate concentration was less than the initial. This decrease in sulfate concentration might have occurred because of a higher solids removal rate during this portion of the duration test. More sulfate would also have been removed in the larger blowdown stream so that sulfates were removed faster than they were formed by oxidation.

Potential Errors In The Estimated Oxidation Rate--

A major concern in evaluating the sulfite oxidation rate was that the quantity of sulfate produced would be small relative to the quantity of sulfate which was present in the absorber system at the start of the test. This could result in the oxidation rate being determined by the difference between two relatively large numbers (*i.e.*, the initial and final quantity of sulfate in the absorber system). However, the quantity of sulfate produced was approximately 65 percent of the quantity of sulfate initially present in the system. As a result, the error associated with the sulfite oxidation rate is on the same order as any error in the estimated quantity of sulfate present in the absorber system.

There are several other potential sources of error in the estimated sulfite oxidation rate. Two of the major sources are:

- inaccurate estimate of the absorber system volume, and
- neglecting SO_3 absorption from the off-gas.

The magnitude of these potential sources of error is examined below.

The principal error associated with the estimated quantity of sulfate present in the system is the total system volume (V_S). The error associated with the system volume is due to the uncertainty concerning the volume of slurry in pipes, pumps, and the scrubber downcomer. The volumes of the reaction tank, clarifier, and clarifier overflow tank were accurately known. Therefore, the error in volume is a positive one (*i.e.*, (V_S) actual $>V_S$). Table 4-6 presents the results of calculations which estimate the sensitivity of the oxidation determination to system volume. As shown, an increase in system volume of 600ℓ only produces a -3.5 percent error in the estimated sulfite oxidation rate. Also, since the error results in a reduction of the estimated oxidation rate the initial estimate of 6.6 percent oxidation is conservative.

TABLE 4-6. SENSITIVITY OF SULFITE OXIDATION RATE TO CHANGES IN ABSORBER SYSTEM VOLUME

V_S(ℓ)	ΔV_S(ℓ)	$V_S+\Delta V_S$(ℓ)	$[SO_4]_P$(gmol)	$\%\Delta[SO_4]_P$
5830	200	6030	645	-1.2%
5830	400	6230	638	-2.3%
5830	600	6430	630	-3.5%

Another possible source of error in the estimated sulfite oxidation rate is the assumption that no $SO_3(H_2SO_4)$ is removed from the off-gas in the absorber. Previous tests indicated an average H_2SO_4 concentration in the flue gas of 0.48 g/Nm^3. Over an 8 hour period, this is equivalent to 156 gmoles of sulfate which may have been removed from the off-gas in the absorber.

Assuming 100 percent removal efficiency for H_2SO_4 results in an estimated sulfite oxidation fraction of 5.0 percent. In other words, the estimated oxidation fraction of 6.6 percent may be in error by as much as -24 percent. While this error appears to be significant, it is unlikely that much SO_3 was removed in the absorber. At the temperature of the off-gas in the absorber,

SO_3 exists as very fine ($\sim$0.1μ) particles which should tend to pass through the absorber. In any event, the potential error again indicates that the estimated oxidation fraction is high and thus a conservative estimate.

4.2.2 Determination of Absorber Stoichiometry

An important criteria in determining absorber performance and accuracy of process measurements is the absorber stoichiometry or the ratio of the moles of $Mg(OH)_2$ fed to the moles of SO_2 removed from the flue gas. Theoretically, this ratio should be 1.0 since 1 mole of $Mg(OH)_2$ is required to react with a mole of $SO_3^=$ thus forming $MgSO_3$. Since the MgO system is regenerable it is not critical that this ratio be exactly 1.0. Any $Mg(OH)_2$ which does not react will eventually be recycled and thus it is not wasted. However, if the ratio is much above 1 this results in an added burden on the solids handling and regeneration system to process unreacted MgO.

The stoichiometric ratio also serves as a check on certain process measurements such as flue gas flow rate, and inlet and outlet SO_2 concentrations. Since the quantity of $Mg(OH)_2$ fed to the system was known accurately, large variations in the stoichiometric ratio, especially below 1.0, would indicate inaccuracies in the process measurements associated with determining the quantity of SO_2 collected during the duration test.

Table 4-7 presents the results of calculations used to estimate the stoichiometric ratio during the duration test. As shown, the stoichiometric ratios calculated for the initial and final 8 hours of the duration test are slightly greater than 1.0. This indicates that there is a close agreement between the $Mg(OH)_2$ feed rate and the SO_2 removal rate calculated from process measurements. Therefore, it appears that the calculated SO_2 removal rate is accurate (±10 percent).

TABLE 4-7. ESTIMATED STOICHIOMETRIC RATIO FOR DURATION TEST

Time period	Average $Mg(OH)_2$ feed rate	Average SO_2 removal rate	Stoichiometric ratio
0-8 hrs	26.8 gmol/min	25.3 gmol/min	1.06
16-24 hrs	21.8 gmol/min	20.2 gmol/min	1.08

Potential Errors in the Estimated Stoichiometric Ratio--

The estimated stoichiometric ratio shown in Table 4-7 is greater than 1.0. There are several possible reasons for this including:

- The calculated SO_2 removal rate is lower than the actual removal rate.
- Less than 100 percent of the $Mg(OH)_2$ reacts with SO_2.

Measurement of gas flow rate and SO_2 removal contains inherent inaccuracies. The DuPont Model 400 photometric analyzer indicated SO_2 concentrations within ±5 percent of the Reich test. Use of an S-type pitot tube provides an accurate measurement (±10%) of gas velocity and the inclined monometer used to measure the pitot pressure drop was accurate to ±5 percent. Therefore, it appears that these errors alone are sufficient to account for the estimated stoichiometry being greater than 1.0.

It also appears, however, that the actual $Mg^{++}/SO_3^{=}$ stoichiometric ratio was greater than 1.0. Analysis of the solids in the bleed stream from the reaction tank consistently indicated Mg^{++} concentrations in excess of the SO_3^{-2} concentrations. Based on this information it appears that the estimated stoichiometric ratios presented in Table 4-7 are representative of the actual absorber stoichiometry.

4.2.3 Results of Material Balance Calculations for the Absorber System

The final objective of the duration test was to develop sufficient data to permit closure of a material balance for the absorber system. Closure of

a material balance with reasonable accuracy (±10 percent) is useful from two standpoints. First, it verifies the accuracy of process measurements, chemical analysis procedures, and sampling techniques. Second, it confirms the reagent ($Mg(OH)_2$) consumption requirements for operation of the system.

In order to complete material balance calculations for an absorption system it is desirable to have process and chemical data from continuous operation at constant conditions. Previous Radian experience has indicated that a test of 100 hours duration is sufficient to provide accurate closure of a system material balance. Unfortunately, the scheduled duration test of the MgO system was terminated after 24 hours with only 10 hours of continuous operation. Nevertheless, an attempt has been made to complete material balance calculations for the final 8 hours of the duration test.

The two species of interest for use in material balance calculations are magnesium and sulfur including both sulfite and sulfate ions. Both magnesium and sulfur are present in the aqueous and solid phases and as a result, chemical analysis of both phases is required. Also, a knowledge of the split between the aqueous and solid phases is necessary. The equation used for computing a material balance around the absorber is:

$$[A]_{IN} + [A]_{INITIAL} = [A]_{OUT} + [A]_{FINAL} \qquad (4\text{-}23)$$

where: $[A]_{IN}$ = gmols of species A added to the system during the test

$[A]_{INITIAL}$ = gmols of species A in the system at the start of the test

$[A]_{OUT}$ = gmols of species A removed from the system during the test

$[A]_{FINAL}$ = gmols of species A in the system at the end of the test

A = magnesium or sulfur

In using Equation 4-23, the sources of addition and removal of magnesium and sulfur from the system must be considered. Magnesium is added to the system as $Mg(OH)_2$ for reaction with absorbed SO_2. Sulfur is added to the system as SO_2 which is captured in the absorber. Both magnesium and sulfur are removed from the system in a bleed stream containing solid and aqueous phases.

Table 4-8 presents the results of material balance calculations for both magnesium and sulfur. As shown, the results of these calculations indicate a substantial error for both species. In the case of magnesium, approximately 4500 gmols or 43 percent of the magnesium added to the system could not be accounted for. For sulfur, about 4600 gmols or 48 percent of the sulfur collected in the absorber could not be accounted for.

TABLE 4-8. RESULTS OF MAGNESIUM AND SULFUR MATERIAL BALANCE CALCULATIONS

Species	IN + INITIAL (gmol)	OUT + FINAL (gmol)	Δ (gmol)	ERROR (Δ/IN)x100
Mg	16,346	11,810	4,536	43%
S	15,073	10,450	4,623	48%
Mg/S	1.08	1.13	0.98	-

Potential Errors in the Material Balance Calculations--

Due to the magnitude of the error in the material balance calculations, very little information can be obtained from the results. However, careful examination of the data in Table 4-8 reveals some general trends in the results. As shown, the quantity of magnesium to sulfur which are unaccounted for are almost exactly equal. This indicates that the error is probably an accounting error and almost certainly not an error in the chemical analyses techniques. Somehow, a quantity of liquid or solid material which has magnesium and sulfur in equimolar quantities was lost or not accounted for during the test. At typical concentrations measured during the test, the missing material could be accounted for by approximately 1000 kg of solids or by 15,000ℓ of liquid.

Because of the higher "concentration" of magnesium and sulfur in the solid phase it appears that unaccounted for solids would be the source of the error. It is very unlikely that an error of 15,000 ℓ (3 times the system volume) could be made, but 1000 kg of $MgSO_3$ solids only occupies a volume equivalent to 580ℓ (about 1/10 the system volume). There are several other reasons to suspect that the majority of the material balance error is due to unaccounted solids. First, the bleed stream removed from the reaction tank was very difficult to sample representatively and there is a strong possibility that the actual solids content was higher than that measured during the duration test. Second, throughout the duration test a buildup of solids on the bottom of the reaction tank was noticed. It was anticipated that this buildup would eventually reach a steady-state level but, unfortunately, the test was terminated before this could occur. After the test was terminated, the reaction tank was examined and a 15 to 20 cm layer of solids was found on the bottom. Approximately 14 cm are required to account for the error in the material balance calculations. Thus, this buildup of solids is probably responsible for the material balance error, although the difficulty in sampling the bleed stream might also have contributed.

Due to the magnitude of the error in the material balance calculations, no other conclusions can be drawn concerning the results. However, based on the results which showed nearly equimolar errors in both magnesium and sulfur species, it appears that the chemical analysis procedures are fairly accurate. An inaccuracy in the procedure for either magnesium or sulfur would have resulted in an error which was not equimolar in both magnesium and sulfur.

4.3 TEST RESULTS NOT RELATED TO ABSORBER PERFORMANCE

The information presented in Sections 4.1 and 4.2 has focused on test results directly related to the performance of the absorber and the ability of the system to remove SO_2. However, there are aspects of the MgO system which must be considered in addition to the performance of the absorber including:

- the type of solids produced (tri- or hexahydrate), and
- process control of the absorber system.

As mentioned earlier, the type of solids produced in the system is an important design consideration for an MgO scrubbing system. As a consequence, the discussion in this section will focus on the type of solids formed in the pilot-scale tests and the factors which influence the type of solids produced. In addition, a discussion of the process control requirements for the pilot-scale absorber is presented. This discussion will center on experiences during the test program.

4.3.1 $MgSO_3$ Solids Formation

In an MgO scrubbing process, $MgSO_3$ solids are formed in the reaction tank, separated from the scrubbing slurry, dried and regenerated to produce MgO for recycle to the process. From previous tests of the MgO system, it has been discovered that $MgSO_3$ can precipitate in the reaction tank in one of two forms; $MgSO_3 \cdot 6H_2O$ and $MgSO_3 \cdot 3H_2O$. Since the two hydrated forms of $MgSO_3$ have different physical properties, the type of hydrate formed affects the design of the solids separation, drying, and regeneration equipment.

Some of the more important design considerations associated with each hydrate are presented in Table 4-9. As shown, neither hydrate has a distinct advantage which would make it the desired product in all applications. The trihydrate forms smaller crystals which are much more difficult to dewater than the hexahydrate. However, because the trihydrate only has three waters of hydration, less energy is required to vaporize the water although higher temperatures are required to dehydrate the trihydrate as compared to the hexahydrate. Problems with formation of dust in the dryer (which removes the waters of hydration as well as the free water) are less with the trihydrate. Dusting occurs when dehydrating the hexahydrate due to a "popcorn" effect as crystals explode when the waters of hydration are driven off. This "popcorn" effect results in the production of a fine dust of $MgSO_3$ which presents operating difficulties in the dryer and calciner.

TABLE 4-9. RELATIVE MERITS OF MAGNESIUM SULFITE HYDRATE FORMS

Hydrate	Advantages	Disadvantages
$MgSO_3 \cdot 3H_2O$	- Less energy to dehydrate	- Poor dewatering properties
	- Reduced dusting during dehydration	- Higher temperature for dehydration
$MgSO_3 \cdot 6H_2O$	- Relatively easy solid/liquid separation	- Dusting problem during dehydration
	- Lower temperature dehydration	
	- Good dewatering properties	

It is evident from the above discussion that a solids handling and regeneration system designed for $MgSO_3 \cdot 3H_2O$ would be substantially different from one designed for $MgSO_3 \cdot 6H_2O$. Since there is no distinct advantage to either hydrate form, the key design consideration is the ability to predict which hydrate will form in the reaction tank. Initially, problems were encountered in predicting the hydrate to be formed in utility applications. Based on pilot-scale tests, a demonstration unit constructed at Boston Edison Company's Mystic power plant was designed to process $MgSO_3 \cdot 6H_2O$ solids. Shortly after the MgO system was started up, the solids produced were hexahydrate. However, after the system had operated for awhile, the crystals changed to the trihydrate. Ultimately, the solids handling and regeneration equipment had to be modified to handle the smaller trihydrate crystals.

At the time the MgO system was designed for the Mystic power plant, the factors which controlled which hydrate would form were not well defined. However, more recent experimental work has identified the factors which control hydrate formation. In order to facilitate understanding of these factors, a discussion of some fundamental aspects of $MgSO_3$ precipitation chemistry is presented here.

For an ideal solution, the solubility product constants for the tri- and hexahydrates can be expressed in terms of their concentrations as shown by Equations 4-24 and 4-25.

$$K_{sp_3} = [Mg^{++}] \cdot [SO_3^{=}] \cdot [H_2O]^3 \quad (4\text{-}24)$$

$$K_{sp_6} = [Mg^{++}] \cdot [SO_3^{=}] \cdot [H_2O]^6 \quad (4\text{-}25)$$

These equations indicate that the solubility of both hydrates is dependent only on the solubility product constant which is a function of temperature.

The relationship between the solubility product constants and temperature is presented graphically in Figure 4-13. Interpretation of Figure 4-13 is straightforward and it can be used to predict which hydrate will form for ideal solutions. For any temperature, the lower of the two solubility curves represents the hydrate which is least soluble or the one which will precipitate from a saturated solution. As shown, the curves for the tri- and hexahydrate cross at about 40°C indicating that hexahydrate should form below 40°C and the trihydrate should form above this temperature.

The above discussion is true only for ideal solutions. Experimental evidence indicates, however, that the solubility of $MgSO_3$ in aqueous solutions is greatly influenced by the presence of other species such as $MgSO_4$, a major component in MgO scrubbing systems. In order to account for this nonideality, it is necessary to calculate the activities of the species in the precipitation reaction and it is useful to redefine the solubility product constants for nonideal solutions.

$$K_{sp_3} = (A^*_{Mg}) \cdot (A^*_{SO_3}) \cdot (A^*_{H_2O})^3 \quad (4\text{-}26)$$

$$K_{sp_6} = (A^*_{Mg}) \cdot (A^*_{SO_3}) \cdot (A^*_{H_2O})^6 \quad (4\text{-}27)$$

The activities shown in Equations 4-26 and 4-27 (A*) are those at equilibrium conditions. These are distinct from the actual activities (A) in a scrubbing solution which are used to define an activity product (AP).

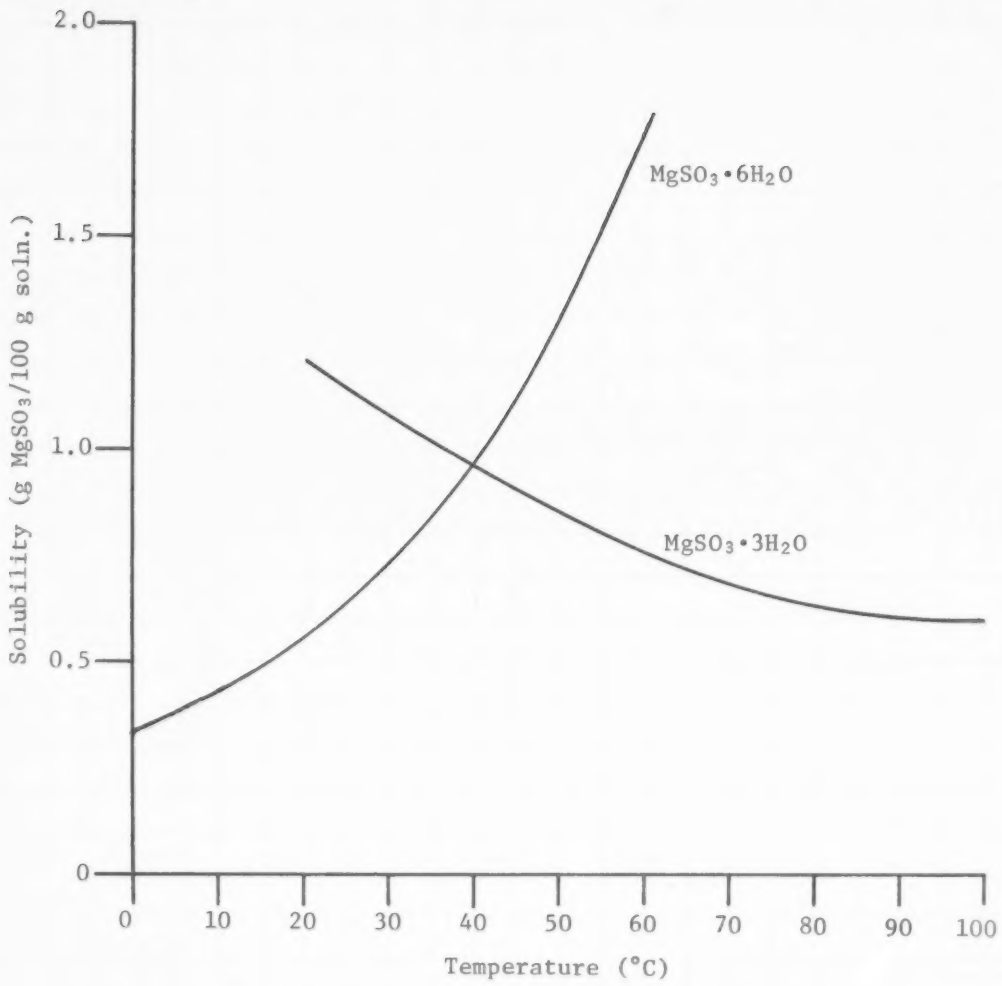

Figure 4-13. Solubility *vs.* temperatures for $MgSO_3$ hydrates.

$$AP_3 = (A_{Mg^{++}}) \cdot (A_{SO_3^{=}}) \cdot (A_{H_2O})^3 \qquad (4\text{-}28)$$

$$AP_6 = (A_{Mg^{++}}) \cdot (A_{SO_3^{=}}) \cdot (A_{H_2O})^6 \qquad (4\text{-}29)$$

The activity product is useful in determining if there is a driving force for precipitation of $MgSO_3$ hydrates and also in determining which hydrate will form in actual scrubber solutions. If the activity product is larger than the solubility product constant, then the solution is supersaturated and, conversely, when the activity product is smaller than the solubility product constant, the solution is subsaturated.

The redefined solubility product constants and the activity product now account for nonideal behavior and can be used to predict which hydrate will form in a scrubbing solution. This is illustrated in Figure 4-14 for changes in solution composition. The ordinate in Figure 4-14 is AP_3, the activity product of $MgSO_3 \cdot 3H_2O$. The hexahydrate solubility properties can be plotted on the same graph since $AP_3 = \frac{AP_6}{(AH_2O)^3}$. The figure shows the two hydrate solubility product constants in terms of AP_3 in solutions of varying composition. As shown, the trihydrate-hexahydrate phase transition temperature decreases with increasing dissolved salt content. As a result, the temperature at which trihydrate is the species formed will decrease as shown.

The curves in Figure 4-14 can be used to predict which hydrate will form in the same manner as Figure 4-13. The lower curve at a given temperature represents the most stable hydrate. However, one additional factor must be considered in evaluating which hydrate will form. Based on laboratory measurements of precipitation rates, the hexahydrate precipitation rate has been determined to be approximately 1000 times greater than that of the trihydrate. As a consequence, for conditions at which the activity product is greater than both K_{sp_3} and K_{sp_6}, tri- and hexahydrate can precipitate although the hexahydrate will predominate due to its more rapid precipitation rate. Conditions under which this can occur are represented by the shaded area in Figure 4-15.

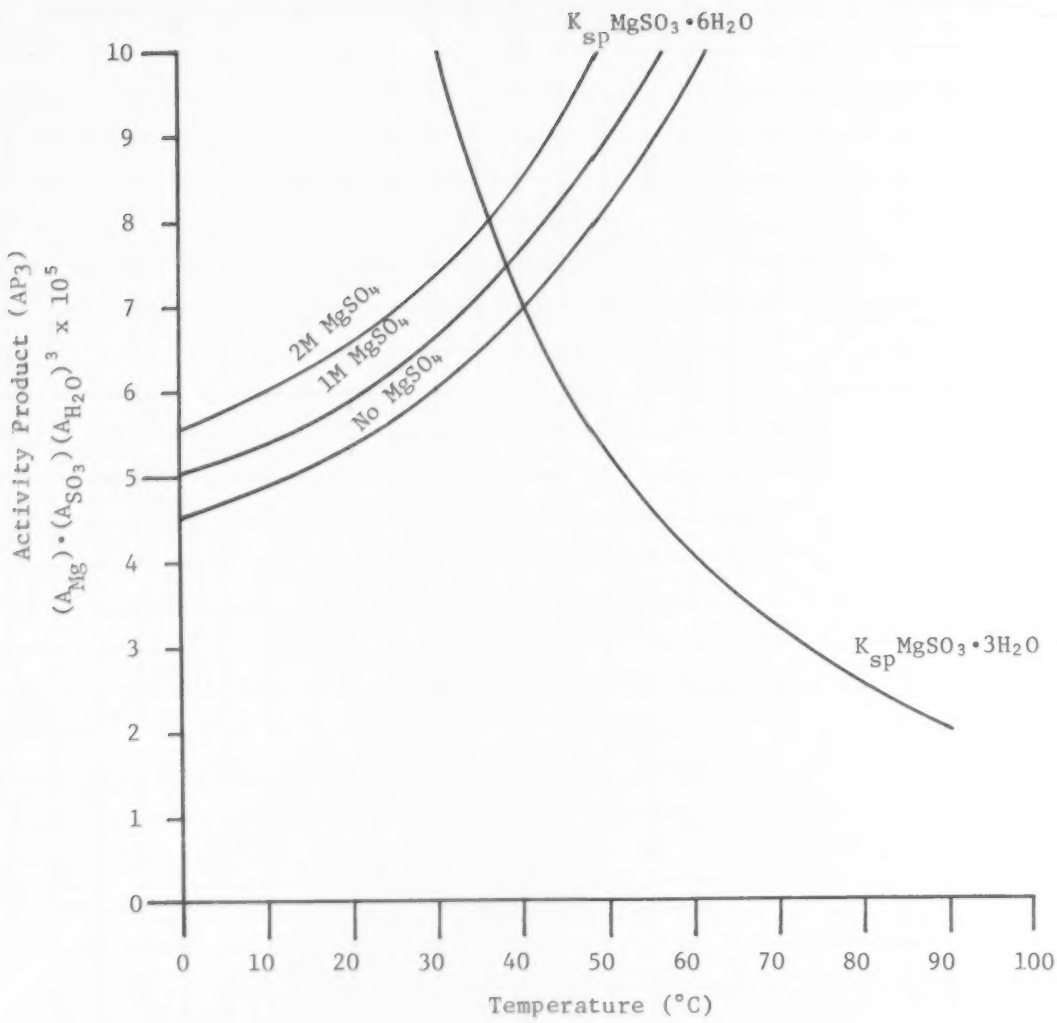

Figure 4-14. Intersection of solubility product constants of $MgSO_3$ tri- and hexahydrates indicating the phase transition temperature in solutions of different compositions.

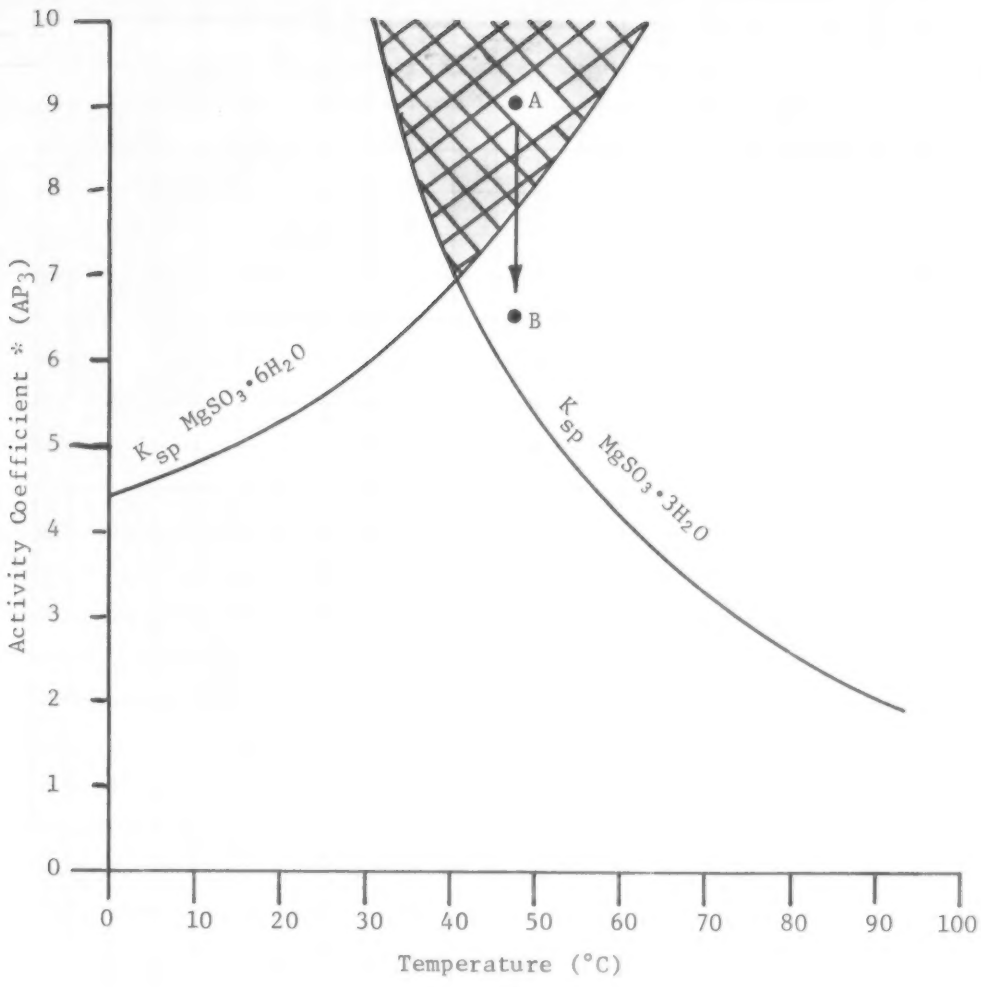

Figure 4-15. Region where solution is supersaturated in both tri- and hexahydrate.

*NOTE: The curves do not represent actual numerical values of the activity products and K_{sp}, but do represent the trend for changes in K_{sp} with temperature.

For a closed or batch system, as the hexahydrate precipitates (Point A), the activity product is lowered until it is below K_{sp_6} (Point B) and then trihydrate precipitation will occur. In a steady-state situation such as a scrubbing system, the activity product is constant and the majority of the solids produced will be hexahydrate.

In the case of the Boston Edison system discussed earlier, the initial solids produced were hexahydrate. After the initial operating period, sulfate buildup caused a change in the K_{sp_6} relative to K_{sp_3} as shown in Figure 4-16. This resulted in a change from hexahydrate to trihydrate formation. For most utility applications, trihydrate would be the expected form due primarily to the temperature at which the scrubber operates.

During the pilot-scale tests at Molycorp, the off-gas entering the absorber was saturated in a quench scrubber and the operating temperature was about 40°C. The point at which the Molycorp system was operated is also illustrated in Figure 4-16. This indicates a potential for both tri- and hexahydrate formation, but due to its relatively rapid precipitation rate the hexahydrate was the only form found in the system.

There are several characteristics of the pilot-scale system tested at Molycorp's plant which led to formation of $MgSO_3 \cdot 6H_2O$. The principal factors are the high SO_2 pickup per unit volume of slurry in the absorber, the dissolution of $MgSO_3$ solids in the absorber, and the relatively low operating temperature of the system. The first two of these factors contribute to a relatively high value for the activity product which caused the hexahydrate relative saturation (AP_6/K_{sp_6}) of the slurry in the reaction tank to be greater than one. The low temperature of the slurry in the reaction tank also contributed to the formation of hexahydrate. Examination of Figure 4-16 indicates that an increase in the reaction tank temperature above about 55°C could reduce the value of AP_3 below K_{sp_6} and thus result in trihydrate rather than hexahydrate formation.

In order to predict which hydrate will form for a particular system design, it is necessary to estimate what the activities of Mg^{++}, $SO_3^{=}$, and

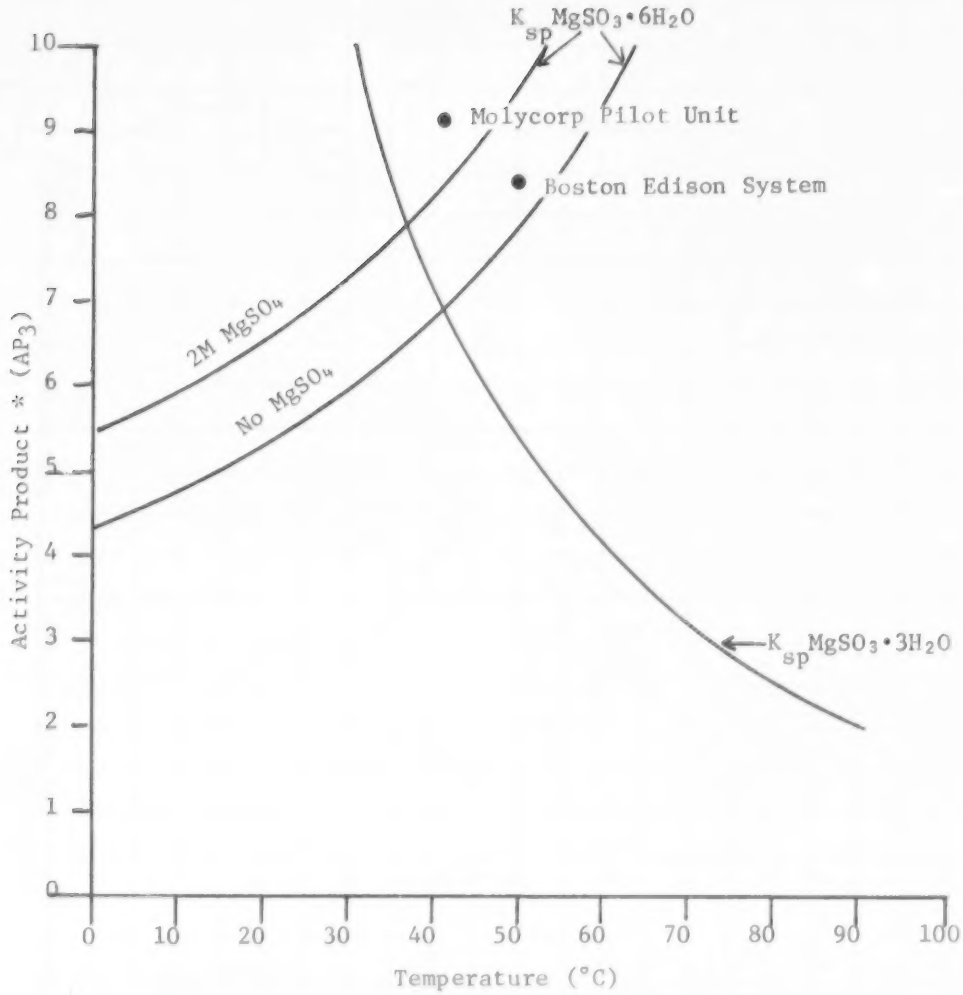

Figure 4-16. Operating conditions for Molycorp pilot unit and Boston Edison utility MgO system.

* NOTE: The curves and points do not represent actual numerical values of the activity products and K_{sp}, but do represent the trend for changes in K_{sp} with temperature and sulfate concentration.

H_2O will be in the reaction tank and then determine the relative saturation of the slurry in the reaction tank with respect to both the tri- and hexahydrate. Estimation of activities in a scrubber solution is a difficult task and requires consideration of all the ionic species in solution. Typically, this requires a computer routine for accurate estimation of activity coefficients. In addition, in order to compute reaction tank concentrations, it is necessary to consider the SO_2 removal, the reaction tank size, and the precipitation rates of tri- and hexahydrate. All these factors will influence the relative saturation of the tri- and hexahydrate in the reaction tank.

Table 4-10 presents some general guidelines which can be used to design a system to produce a specific hydrate in the reaction tank. For more detailed information including precipitation rate data, the reader is referred to a study entitled "Precipitation Chemistry of Magnesium Sulfite Hydrates In Magnesium Oxide Scrubbing."[4] This study includes experimental data which can be useful in design of an MgO system for precipitation of a specific hydrate form.

TABLE 4-10. DESIGN CONSIDERATIONS FOR PRODUCING MAGNESIUM SULFITE TRI- OR HEXAHYDRATE

Design Consideration	Level Which Favors	
	Trihydrate	Hexahydrate
Temperature	High	Low
Dissolved Solids - $MgSO_4$(aq)	High	Low
SO_2 Removal	Low	High
Reaction Tank Size	Large	Small
Weight Percent Solids	High	Low

4.3.2 Process Control of the Absorber System

The ability to control absorber operating parameters at specified levels is an important aspect of any FGD system. The discussion presented here describes several aspects of controlling an MgO system including:

- sorbent feed rate, and
- system turndown.

This discussion is based on experience with the pilot-scale absorber and the results of the short- and long-term tests. For a discussion of previous experience with process control for MgO systems, the reader is referred to reports on the utility demonstration tests which are included in the references of this report.

Control of Sorbent Feed Rate--

Control of the sorbent feed rate can present a significant operating problem in some FGD systems. However, in the MgO scrubbing process, and the pilot system in particular, this was not the case. Over the pH range examined during the test program, the reaction tank pH was used as feedback signal for controlling the sorbent feed rate. Use of the reaction tank pH provided an accurate measure of the sorbent requirements of the system. This was evidenced by several results, principally the fact that the estimated stoichiometric ratio during the duration test was close to 1.0. This indicates that the sorbent feed rate was approximately equal to the SO_2 absorption rate. Since the feed rate was adjusted to maintain a constant reaction tank pH, the pH was an accurate measure of the sorbent requirements of the system.

Based on the results of the test program it appears that the pH will provide an accurate feedback mechanism for controlling the MgO feed rate to the system. However, it must be emphasized that this is only true for the pH range examined during the test program. Use of pH on a larger scale MgO scrubbing system should provide adequate process control of the sorbent feed rate. This represents technology available in the utility industry and it should be relatively easy to implement.

System Turndown--

The ability of a scrubbing system to operate at reduced gas flow rates or to turndown is an important aspect of process control. Based on the results

of the pilot-scale tests, the MgO system has exhibited excellent turndown capability. Recalling the design equation developed in Section 4.1, the test results demonstrated that the SO_2 removal efficiency was unaffected by gas flow rate over the range of gas velocities tested (*i.e.*, 1.8 to 2.6 m/sec). Therefore, for a system design to operate with a gas velocity of 2.6 m/sec at full gas flow rate, it can be turned down to 70 percent of full flow without any impact on SO_2 removal efficiency and without requiring corresponding changes in slurry feed rate to the absorber. In addition, it is possible that the absorber can turn down even further with no decrease in removal efficiency. Further tests are required to determine how much gas velocity can be reduced before performance of the absorber is affected.

For multiple absorber systems, the ability of the system to turn down can be extended even further. Using three absorbers, for example, flow to each absorber can be reduced to 70 percent. At this point, the gas flow could be diverted to two absorbers, while isolating one, thus providing 67 percent capacity at design gas velocity. Flow through the two operating absorbers could then be reduced to 70 percent for a net turndown below 50 percent of full design gas flow.

Because gas flow rate can be reduced without necessitating changes in liquid flow rate and without impacting the SO_2 removal efficiency of the system, the MgO system tested (*i.e.*, using a packed absorber) is well suited to applications which experience fluctuations in gas flow rate. By careful design of the system including the use of multiple absorbers, the turndown capability can be extended below 50 percent of design capacity.

4.4 COMPARISON OF TEST PROGRAM RESULTS TO PREVIOUS TEST WORK

Previous development of the MgO system has been conducted for utility applications. Test work which has been well documented includes:

- testing on an oil-fired boiler at Boston Edison Company's Mystic Station,[5] and

- testing on a coal-fired boiler at Potomac Electric Company's Dickerson Generating Station.[6]

In order to put the pilot tests conducted at Molycorp into perspective, this section presents a comparison of the pilot-scale tests with the results of the utility test programs.

The pilot-scale test program differs from previous utility test programs in several respects. The most significant difference between the Molycorp pilot-scale tests and the utility test programs is the fact that the utility demonstration units were integrated systems, containing both absorption equipment and solids regeneration equipment. Since many of the problems encountered during the utility tests were associated with solids handling and regeneration equipment, the reader is cautioned that this may make the results of the pilot-scale tests appear more favorable by virtue of the pilot unit's relative simplicity. However, other differences in the two applications, particularly the absorber design, do indicate that the pilot-scale absorber tested exhibits superior performance for applications with high SO_2 concentrations.

Table 4-11 compares some of the absorber operating parameters for the two utility demonstration units with the same parameters for the pilot-scale absorber. It should be noted that both utility applications employed venturi-type absorbers as compared to the packed absorber used in the pilot tests. The parameter levels presented for the pilot absorber are those selected and tested in the duration test. The levels presented for the Boston Edison System are based on a material balance presented in the final report for that demonstration. The parameter levels shown for the Potomac Electric System were selected as representative from a series of test results presented in the final test report for that program.

As shown in Table 4-11, the performance exhibited by the pilot-scale absorber was generally superior to the utility demonstration units in several respects. The liquid-to-gas ratio for the pilot unit is approximately 20 to 25 percent of that for the other systems, resulting in smaller pumps and

TABLE 4-11. PERFORMANCE COMPARISON OF PILOT ABSORBER AND UTILITY DEMONSTRATION-SCALE SYSTEMS

System	Gas Flow Rate (Nm^3/hr)	L/G Ratio (ℓ/Nm^3)	Gas Velocity (m/sec)	Absorber Feed pH	Absorber ΔP (kPa)	SO_2 Removal Efficiency
Boston Edison	723,000	4.8	3.0[1]	7.3	1.74	90
Potomac Electric	<174,000	4.4	NA	7.0	1.84	81
Molycorp	4,000	0.9	2.6	7.8	0.75	92

[1]Estimated based on absorber diameter of 9.5M.

lower pumping costs for the absorber system. In addition, the pilot-scale absorber pressure drop is about 40 to 45 percent of the pressure drop measured for the other systems. This corresponds to an equivalent reduction in fan power requirements for overcoming the absorber pressure drop. Finally, the SO_2 removal efficiency in the pilot absorber was equal to or better than the removals attained by the utility systems even though the SO_2 concentration was 5 times greater. However, outlet SO_2 concentrations from the pilot absorber should be maintained above 500 ppm to prevent plugging of the absorber by $MgSO_3$ solids, while outlet SO_2 concentrations of about 100 ppm and less than 350 ppm were achieved by the utility systems. Also, the operating gas velocity for the pilot absorber was about 15 percent lower than for the other systems which would result in the requirement for an absorber which is approximately seven percent larger in diameter using the packed configuration.

It should be noted that the performance of the pilot absorber was such that it may not be applicable to a utility situation. At very low outlet SO_2 concentrations, the absorber tends to plug with $MgSO_3$ solids and this is a situation which would be likely to occur in a utility application. However, it does not appear likely that the absorbers employed in utility designs would be suitable for use on gas streams containing 0.5 to 1.0 percent SO_2. The available test data indicate that the removal efficiency of venturi absorbers declines at elevated SO_2 concentrations.

In summary, the pilot-scale absorber tested at Molycorp exhibited superior performance when compared to previous utility tests of the MgO system. A scale-up of the pilot system for application to a primary nonferrous smelter off-gas would be expected to provide better SO_2 removal efficiency at lower operating cost levels than the designs employed for the utility demonstrations.

4.5 OPERATIONAL ISSUES NOT ADDRESSED DURING THE TEST PROGRAM

The results of the pilot-scale tests conducted at Molycorp's Washington, PA facility can be used in designing an MgO scrubbing system for similar applications. In particular, Equation 4-19 is a useful tool for specifying an absorber design for application to weak SO_2 off-gas streams from primary

nonferrous smelters. However, due to limitations of equipment, time, and resources, there are several issues that were not addressed during the test program but which must be considered in applying the MgO system to a weak SO_2 off-gas. The most significant of these issues are:

- regneration of MgO reagent from product $MgSO_3 \cdot 6H_2O$, and
- effects of closed loop operation on absorber performance.

4.5.1 Regeneration of MgO From $MgSO_3$

The process of regenerating MgO from $MgSO_3 \cdot 6H_2O$ which is produced in the absorber-reaction tank system is relatively straightforward. This process involves dewatering, drying, and calcining the $MgSO_3$ solids. As discussed earlier, the regeneration process design depends only on the type of solids (tri- or hexahydrate) produced with the design being substantially independent of the source of the solids. Therefore, it would be expected that the solids handling and regeneration system designs developed for application to the utility industry would be directly applicable for use in the primary nonferrous metals industry. This is especially true because the MgO regeneration step produces a concentrated SO_2 stream which is suitable for processing in a sulfuric acid plant similar to those currently in use in the primary nonferrous metals industry. However, there is one aspect of MgO regeneration which could present problems in application of this technology to the primary nonferrous metals industry.

Because the MgO system is regenerable, its operation is essentially a closed loop. As a result, any compounds which enter the system in the gas stream can be concentrated until the loss from the system equals the rate at which a compound enters. Previous experience indicates that MgO losses from the system range from 2 to 5 percent of the total MgO present. Assuming that other compounds are lost from the system at an equivalent rate, then those compounds can concentrate 20 to 50 times in the circulating slurry. Off-gas streams in the nonferrous metals industry typically contain trace quantities of certain elements such as mercury, lead, etc. If these elements enter an

MgO system, they can concentrate and potentially cause problems in the regeneration step.

The calciner used to regenerate the MgO typically operates at 1000°C. At this temperature, many of the elements which can concentrate in the system are volatile and they can be present in the off-gas from the calciner. If this off-gas is to be processed in a sulfuric acid plant it would be necessary to treat it for removal of any particulates or compounds which could poison the catalyst used in the sulfuric acid plant. This would necessitate additional equipment to treat the off-gas from the calciner and it must be included in the design of an MgO acid plant concentrating system.

As an alternative, the gas entering the absorber could be treated to remove particulates and any other elements or compounds which may eventually be discharged in the calciner off-gas. This alternative is more attractive from an overall design and safety standpoint than treating the calciner off-gas. By removing trace elements and particulates upstream of the absorber, these compounds will not concentrate in the recirculating slurry. This will eliminate potential corrosion problems and it will also eliminate a potentially serious pollution problem in the event of an unexpected discharge of slurry from the system.

The location, type, and design of equipment to collect trace elements is, of course, the option of the system designer. However, it is recommended that this equipment be located upstream of the absorber and that it include a wet scrubber to quench the gas before it enters the absorber. This type of system will be mandatory if the off-gas is at high temperatures or if the gas stream contains significant quantities of chlorides, which can build up and cause serious corrosion problems in the system. In situations where the gas stream entering the absorber is cool and it does not contain potentially corrosive compounds, it should be possible to treat the calciner off-gas. In any event it will be necessary to collect any trace elements or other compounds which can poison the catalyst used to produce sulfuric acid in the regeneration process.

4.5.2 Effects of Closed Loop Operation on Absorber Design

During the pilot-scale test program, the absorber was operated open loop with respect to MgO and water. Open loop operation with respect to MgO was due to the fact that the pilot unit did not include equipment to regenerate $MgSO_3$ solids. The system was operated open loop with respect to water due to the inability of the clarifier to concentrate the $MgSO_3$ solids above 35 wt percent. The impact of closed loop operation on MgO regeneration was discussed in the previous section. This section presents a discussion of the impact of closed loop operation on the design and operation of the absorber. The key issues which must be addressed in considering closed loop are:

- sulfate buildup in the absorber, and
- calcium buildup in the absorber.

The following discussion examines each of these issues and identifies their impact on absorber operation and design.

Sulfate Buildup--

In a fully integrated MgO scrubbing system, $MgSO_4$ would be expected to build up in the scrubbing liquor until the liquor becomes supersaturated and $MgSO_4$ begins to precipitate. In an MgO scrubbing system, this occurs when the scrubbing liquor is about 20 wt percent $MgSO_4$ which is equivalent to a sulfate concentration of 1.7 gmol/ℓ.

During the pilot-scale tests, no sulfate precipitation was observed due to the fact that the system was operated open loop. In fact, the aqueous phase sulfate concentration ranged from 0.14 to 0.36 gmol/ℓ which is well below the concentration of a saturated solution. As a result, the concentration of sulfate during the pilot-scale tests was not representative of the concentrations in a full-scale system and it is possible that this discrepancy could impact the ability of the design equation to predict SO_2 removal efficiency.

The design equation developed in Section 4.1 employed pH as a measure of liquid phase alkalinity in the absorber feed although the alkaline species in the scrubbing liquor was $SO_3^=$. The reason pH served as an adequate measure of alkalinity was the fact that during the test program, the concentration of $SO_3^=$ in the scrubbing liquor remained relatively constant. Thus, pH was an indicator of the relative concentrations of $SO_3^=$ and HSO_3^- rather than an absolute measure of liquid phase alkalinity. Any significant changes in aqueous phase $SO_3^=$ concentration from those measured during the pilot-scale tests could result in SO_2 removal efficiencies which are not accounted for by the absorber design equation.

As previously discussed, changes in the scrubbing liquor concentration due to an increase in $MgSO_4$ can change the solubility of the $MgSO_3$ hydrates and actually change the type of hydrate formed in the system. As a consequence, it is possible that sulfate buildup in the recirculating slurry can significantly change the aqueous phase $SO_3^=$ concentration and, therefore, limit the effectiveness of the design equation in predicting SO_2 removal efficiency for a particular absorber design.

In order to quantitatively assess the impact of increased $MgSO_4$ concentration on the aqueous phase sulfite concentration, it would be necessary to conduct tests at elevated $MgSO_4$ concentrations. However, the magnitude of this impact can be estimated using Radian's aqueous equilibrium program which predicts equilibrium concentrations of inorganic species in scrubber solutions. This program is particularly useful because it accounts for nonideal behavior in concentrated solutions.

The equilibrium program was used to simulate the effect of adding $MgSO_4$ to the reaction tank during one of the short-term variable tests. The results of that simulation are presented in Table 4-12. The aqueous sulfate concentration was raised from 249 mmol/1000 gm H_2O observed in the test program to just over 2000 mmole/1000 gm H_2O in the simulation, nearly an order of magnitude increase. It might be expected that such a large increase in sulfate concentration with a corresponding increase in magnesium concentration would cause a large decline in the aqueous phase sulfite concentration. The results

of the simulation indicate that the sulfite concentration will decline but not as much as the magnesium concentration increases.

TABLE 4-12. EFFECT OF INCREASED $MgSO_4$ CONCENTRATION ON CONCENTRATION OF SULFITE SPECIES IN SOLUTION

Species	Test data concentrations (mmol/1000 gm H_2O)	Simulation concentrations[1] (mmol/1000 gm H_2O)
$SO_4^=$	130	659
$MgSO_4$	119	1345
Total SO_4 ($SO_4^=$ + $MgSO_4$)	249	2004
$SO_3^=$	16	4
$MgSO_3$	119	93
Total SO_3 ($SO_3^=$ + $MgSO_3$)	135	97

[1]Assumes constant relative saturation with respect to $MgSO_3 \cdot 6H_2O$

The equilibrium program predicted a decline in the aqueous phase sulfite concentration of 28 percent for the test conditions examined. However, it is uncertain how significant this decrease is in terms of the SO_2 removal efficiency which would be expected at higher sulfate concentrations. During the short-term variable tests, the aqueous phase sulfite concentration varied ±25 percent from a mean value of 120 mmoles/ℓ and analysis of the data indicated no significant dependence on sulfite concentration. Therefore, it is possible that the decline in sulfite concentration due to increased sulfate concentration may not have a significant effect on SO_2 removal efficiency. However, since increased aqueous phase sulfate concentrations will reduce sulfite concentrations, a major source of alkalinity in the MgO system, the SO_2 removal efficiency may also decline.

In using the design equation developed in Section 4.1 it may be necessary to take a conservative approach due to the impact of increased sulfate concentration. The effect of increased sulfate concentration can be offset by providing additional liquid phase alkalinity in the absorber. The simplest method for doing this is to increase the liquid feed rate to the absorber. An

increase in the liquid feed rate of 25 to 30 percent would be required to offset the decrease in sulfite concentration.

Calcium Buildup--

In addition to sulfate, calcium would also be expected to build up in the recirculating scrubber slurry of a closed loop MgO system. Calcium can enter the system in water used as makeup for water evaporated during gas cooling. The ultimate quantity of calcium in the system will depend on how calcium is removed. At the expected sulfate concentrations in a closed loop MgO system (Table 4-12), any calcium in the system should exist as inert calcium sulfate which will be removed from the system in the same manner as MgO (*i.e.*, through fugitive losses). Since the calcium is expected to exist as an inert solid, its buildup in a closed loop system should not present any operating problem and it should not impact SO_2 removal efficiency.

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APPENDIX A

SAMPLING AND ANALYTICAL PROCEDURES

The sampling and analytical procedures which were used during the pilot-scale tests can logically be divided into two categories: those used to measure gas properties and those used to measure slurry properties. The discussion which follows presents the details of each procedure used during the pilot program. In cases where standard instruments are employed, the discussion is general and the reader is referred to the instrument operating manual.

PROCEDURES USED TO MEASURE FLUE GAS PROPERTIES

Table A-1 identifies the gas properties which were measured during the test program along with the techniques used to make the measurements. Each of these measurement techniques are described below.

TABLE A-1. OFF-GAS MEASUREMENTS AND MEASUREMENT PROCEDURES

Measurement	Procedure
SO_2 Concentration	DuPont Model 400 Reich Test
Moisture	Wet Bulb Temperature
O_2, CO_2	Orsat Analyzer

SO_2 Concentration

Measurement of off-gas SO_2 concentration was very important in terms of documenting the performance of the pilot unit. For the most part, a DuPont photometric analyzer was used to make the measurements. This analyzer relies

on the ability of SO_2 to absorb light at 280 nm. With the appropriate electronic processing, the instrument produces a signal which is proportional to the concentration of SO_2 in a gas sample. The instrument is an extractive monitor through which flue gas continually flows. For more details the reader is referred to the instruction manual for the DuPont Model 400.

As a check on the accuracy of the DuPont monitor, the Reich test for SO_2 was periodically used. This test depends on the reaction of sulfur dioxide with a measured amount of standard iodine solution. The volume of gas is measured with a wet-test meter and the starch iodine end point is used. A detailed description of this technique is presented below.

The sampling equipment for the Reich test includes a 250 ml bubbler, a wet test meter with thermometer and U-tube manometer, and a vacuum or sample pump. The equipment is assembled and connected with rubber tubing as follows. The bubbler is fitted with two glass tubes, a long one reaching nearly to the bottom of the gas sampling line, and a short tube connected by rubber tubing to the gas meter. The rubber tubing between the sampling probe and the bubbler contains a pinch clamp which keeps the solution in the bubbler from being drawn into the duct if the duct has a negative pressure. The gas meter contains a thermometer and a U-tube mercury manometer with the outlet of the meter connected by rubber tubing to the suction end of the vacuum pump. The rubber tubing between the gas meter and vacuum pump contains an adjustable pinch clamp for maintaining proper gas sampling rate. When the tubing connections have been made, the apparatus is ready for use.

The procedure for conducting the Reich test is as follows. Fill the 250 ml bubbler about three-fourths full with DI water and add 2-3 ml of starch indicator solution. Add 0.1 N iodine solution dropwise to the flask, shaking well after each drop, until a definite faint blue color appears and persists. This color will be the end point at the finish of the test. It is not necessary to use fresh water and starch each time a test is to be made. The same water may be used for several tests provided that the solution is adjusted to the faint blue end point color just before each test.

Depending on the sulfur dioxide content of the gas to be tested, 0.10, 0.50, 1, 2, or 10 ml of 0.1 N iodine solution is accurately pipetted into the adjusted solution in the flask. It is now ready for the test.

After the gas sampling line has been thoroughly purged, close the purge valve and assemble the testing apparatus as previously described. Start the vacuum pump and remove the pinch clamp between the bubbler and the sampling probe, then open the adjustable pinch clamp slowly until the gas is bubbling at a rate of .03-.05 ft^3/min (mild bubbling).

The solution in the flask at the beginning of the test is very dark and no change in color will be noticed until the iodine is nearly exhausted. The temperature and pressure differential at the meter should be recorded at this time. As soon as a reduction in color begins to take place, reduce the rate of gas flow by closing down on the pinch clamp. The gas should now be admitted very slowly until the faint blue end point color is reached.

Moisture

The moisture in the off-gas entering the absorber was determined periodically for use in gas flow rate calculations and for use in estimating water losses due to evaporation. The technique used for determining moisture content of the gas was to measure the wet bulb or saturation temperature of the gas. This can be done by inserting a standard recovery thermometer with a wetted wick into the flue gas. Once the wet bulb temperature is determined, the moisture content of the gas can be estimated using a psychrometric chart.

O_2, CO_2

Measurement of O_2 and CO_2 in the off-gas was made periodically for use in gas flow rate calculations. Determination of the O_2, and CO_2 concentrations in the gas was made using an Orsat apparatus. The operating principle of this method consists of subjecting a measured volume of gas sample to successive contact with chemical solutions which serve to absorb specific components, such as carbon dioxide, oxygen, and carbon monoxide from the

mixture. The percentage of the particular component in the mixture is calculated from the decrease in volume of the sample after each contact. For detailed instructions for taking the sample, measuring the sample, absorbing the component and measuring the volume, the reader is referred to the Orsat operating instruction manual prepared by Burrell Corporation.

PROCEDURES USED TO MEASURE SLURRY PROPERTIES

Table A-2 identifies the slurry properties which were measured during each test conducted with the pilot unit at Molycorp. The table also identifies the analytical procedures which were used to make the measurements. Each of these analytical procedures are described below.

TABLE A-2. SLURRY PROPERTIES MEASURED AND ANALYTICAL PROCEDURES USED FOR THE MOLYCORP TEST PROGRAM

Property	Procedure
Wt % solids	Filtration, drying
Temperature	Thermometer
pH	pH meter
Sulfite	Titration
Magnesium	Ion chromatograph
Total sulfur	Ion chromatograph
Chlorides	Ion chromatograph

Weight Percent Solids

Measurement of weight percent solids was required to characterize the scrubbing slurry. This measurement was made on both the absorber feed stream and the absorber bottoms. The procedure for determining the weight percent solids requires filtering and weighing the solids collected from a known weight of slurry. The equipment required includes a volumetric flask, a top loading balance, a vacuum pump-suction assembly, and a Buchner funnel. This equipment is assembled as shown in Figure A-1.

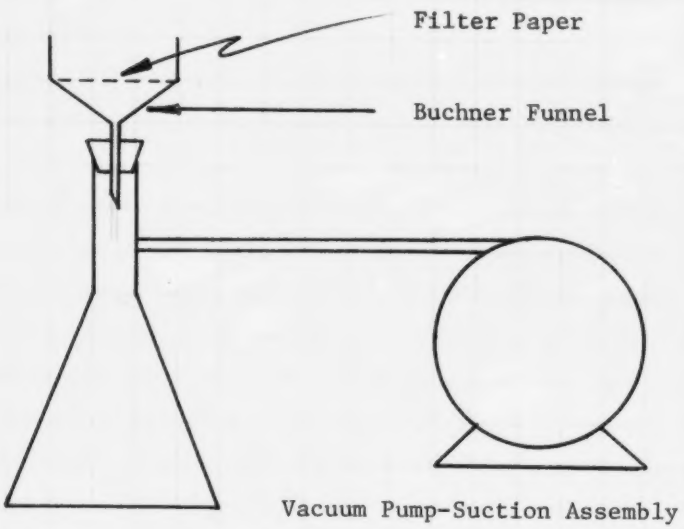

Figure A-1. Equipment for measuring weight percent solids.

The procedure for determining the weight percent solids is as follows. Weigh the volumetric flask to 0.01 g. At the sampling location, fill the volumetric flask with slurry. Weigh the flask to 0.01 g. Filter the slurry through 11 cm Whatman filter paper (weighed) using a suction assembly. Wash the solids with acetone and dry at 40-50°C. Weigh the solids and transfer to a 2 oz. plastic bottle. These solids are then used for sulfite, total sulfur, carbonate, and magnesium analyses.

Temperature

The temperature of the slurry will be measured for each sample using a standard mercury thermometer. The slurry temperature is required to adjust the pH meter and it is also useful in determining the solubility of various chemical species in the slurry.

pH

pH which is a useful measure of alkalinity in the slurry was measured for each slurry sample taken during the test program. The equipment used for measuring pH consisted of a combination pH electrode connected to a pH meter. The pH electrode/meter combination was calibrated daily using 3 standard buffer solutions. For more details the reader is referred to a pH meter/electrode instruction manual.

Sulfite

Sulfite was determined for both the aqueous and solid phases of the slurry samples. The procedure used in both cases was similar, the principal difference being that the solid phase sulfite was dissolved prior to analysis. However, since there are some other differences in the analytical procedures, both solid and aqueous phase sulfite analyses are discussed here for clarity.

Aqueous Phase Sulfite--

Table A-3 lists the equipment and reagents required for the aqueous phase sulfite analysis. The procedure for conducting this analysis is as follows. Pipet 5 ml of iodine solution and add 40-50 ml of sodium acetate buffer into a glass bottle containing a stir bar. Weigh the bottle to 0.01 g. Use the Millipore filter and peristaltic pump to draw a sample stream from the process stream. Fill the bottle with the filtered stream until most of the iodine is reacted. Leave enough volume for the back titration step. Replace the cap and shake. Weigh the bottle again to 0.01 g and back titrate with standard sodium thiosulfate to the starch end point.

TABLE A-3. MATERIALS REQUIRED FOR AQUEOUS SULFITE ANALYSIS

Equipment Required	Reagents Required
Clear glass bottles	pH 6 sodium acetate buffer
Stir bar	.1 N iodine
Top loader balance	.1 N sodium thiosulfate
Millipore filters and stand	Starch solution
Peristaltic pump	
Buret	
Magnet stirrer	

Solid Phase Sulfite--

The equipment and reagents required for the solid phase sulfite determination are similar to those used for aqueous phase sulfite. Consequently, only the procedure is presented here. The first step in the procedure is to weigh 0.05 g of solid sample (obtained from the wt % solids determination) to the nearest 0.1 mg. Then, pour 60 ml of pH 6 buffer solution into a 250 ml small mouth glass bottle. Pipet 10 ml of 0.1 N iodine into the bottle and add the weighed solid sample immediately. Stir for 15 minutes to dissolve the solid sulfite. At the end of the dissolution period begin to titrate with standardized sodium thiosulfate to a starch end point. Blanks should be run using the above procedure without the addition of a sample.

Magnesium, Total Sulfur and Chlorides

Measurement of magnesium, total sulfur and chloride was made using a Dionex Ion Chromatograph. The operation of this instrument is similar in principal to a gas chromatograph. Standards are injected into the instrument and peak heights and retention times are measured. A calibration curve is then drawn for the standards. The sample is injected into the instrument and the peak height is compared to the calibration curve and the concentration determined. For more specific details of how this instrument operates, the reader is referred to the operating manual for the Dionex Ion Chromatograph.

APPENDIX B

TEST DATA FROM THE MOLYCORP PILOT PLANT

This appendix presents the process and chemical data collected during the short-term variable tests. In some cases the data presented has been reduced (e.g., gas flow rates are presented as opposed to pitot tube ΔP readings). The data contained in this appendix represents the input to the model developed and described in Section 4.0 of the main report. No other data were used in developing the empirical constants in the design equation.

TABLE B-1. CONTROLLED VARIABLES - TEST CONDITIONS

Test Number	Flue Gas Flow Rate (scfm)	Liquid Flow Rate (gpm)	L/G Ratio (gal/1000 scf)	Reaction Tank pH	Packing Depth (inches)	Inlet Flue Gas	
						Temperature (°F)	SO_2 Conc. (ppmv)
1	1678	7.8	4.6	7.58	20	102	8674
2	1770	15.7	8.9	7.41	20	100	7414
3	1769	24.4	13.8	7.58	20	102	7457
4	2102	9.1	4.3	7.48	20	103	8200
5	2093	19.0	9.1	7.54	20	101	8093
6	2106	30.3	14.3	7.48	20	102	8200
7	2431	10.2	4.2	7.52	20	105	8047
8	2434	23.0	9.4	7.54	20	103	8309
9	2430	30.6	12.6	7.60	20	104	7837
10	1773	6.2	3.5	7.60	50	100	8756
11	1772	14.8	8.4	7.48	50	102	8123
12	1771	22.1	12.5	7.42	50	104	7822
13	2094	7.9	3.8	7.44	50	103	6234
14	2108	13.3	6.3	7.48	50	100	7616
15	2093	18.0	8.6	7.58	50	101	8514
16	2491	9.4	3.8	7.50	50	105	7986
17	2420	16.9	7.0	7.39	50	104	8466
18	2431	21.0	8.6	7.48	50	105	8078
19	2433	9.4	3.9	6.57	50	103	8594
20	2429	9.4	3.9	5.84	50	103	6883
21	2434	9.4	3.9	7.48	50	103	6030
22	2434	9.4	3.9	7.52	50	103	4605
23	2434	9.4	3.9	7.52	50	103	2354
24	2626	26.9	10.2	7.50	50	96	8093
25	2439	14.3	5.9	7.48	20	102	8674
26	2434	38.5	15.8	7.52	20	103	7748
27	2435	13.8	5.7	7.44	50	104	9260
28	1764	24.4	13.8	6.46	20	103	9885
29	2433	9.4	3.9	7.46	50	103	9190
30	2434	9.4	3.9	7.39	50	103	8200

TABLE B-2. RESPONSE VARIABLES - TEST RESULTS

Test Number	Reaction Tank Temperature (°F)	Absorber Pressure Drop (inches H_2O)	Outlet Flue Gas		SO_2 Removal Efficiency (%)
			Temperature (°F)	SO_2 Conc. (ppmv)	
1	108	1.5	104	4891	44
2	102	0.8	97	3152	57
3	110	0.9	99	2422	68
4	-	1.7	96	4639	43
5	-	-	-	2827	65
6	-	-	-	2392	71
7	117	2.3	104	4104	49
8	114	1.7	104	2848	66
9	116	2.3	103	1875	76
10	98	1.7	101	2354	73
11	86	1.2	94	956	88
12	110	1.3	105	342	96
13	-	1.7	-	1409	77
14	97	1.8	99	382	95
15	116	2.3	104	170	98
16	118	2.8	105	1715	79
17	116	4.1	103	428	95
18	-	-	105	264	97
19	116	2.5	107	3887	55
20	91	1.9	99	3822	44
21	-	-	-	472	92
22	106	2.8	92	230	95
23	103	3.1	94	85	96
24	108	5.8	98	144	98
25	116	-	105	4006	54
26	109	3.2	103	463	94
27	114	2.9	104	850	91
28	-	1.2	-	4526	54
29	114	2.9	107	2035	78
30	103	2.6	102	1547	81

TABLE B-3. CHEMICAL ANALYSIS RESULTS - SCRUBBER FEED SLURRY

Test Number	Temp. (F°)	pH	Solids Content (Wt %)	Aqueous Phase Concentration (mmol/ℓ)				Solid Phase Concentration (mmol/g)		
				Mg^{+2}	SO_3^{-2}	Total Sulfur	Cl^-	Mg^{+2}	SO^{-2}	Total Sulfur
1	102	7.81	7.76	297	105	349	-	5.76	1.77	4.06
2	99	7.70	4.97	388	100	367	-	5.22	4.21	4.44
3	106	7.77	3.17	403	120	338	-	5.37	4.18	4.25
4	86	8.03	4.04	431	91	417	-	6.15	3.91	4.02
5	111	7.82	6.60	397	137	386	-	7.01	3.73	3.63
6	106	7.76	3.43	271	110	320	11.1	6.63	3.85	3.75
7	115	7.74	3.81	416	140	356	-	5.98	4.10	4.05
8	111	7.85	3.70	405	140	355	12.5	6.11	3.85	3.87
9	113	7.83	3.66	873	140	384	-	8.10	3.53	3.57
10	97	7.99	10.40	282	92	337	13.5	5.99	3.77	4.00
11	91	7.77	4.4	372	95	455	-	5.84	4.26	4.37
12	111	7.71	5.22	406	127	353	13.1	4.93	4.41	4.45
13	99	8.03	4.75	443	109	433	-	5.40	*	4.28
14	95	7.99	7.92	238	92	236	-	6.35	3.83	4.15
15	113	7.87	4.99	396	131	391	-	7.69	5.48	6.31
16	117	7.76	6.22	417	136	285	-	5.64	3.99	4.20
17	113	7.73	10.30	400	128	288	16.3	5.10	3.36	4.51
18	115	7.74	4.97	407	136	361	-	5.84	4.04	4.21
19	111	6.63	5.56	328	157	314	-	4.20	4.56	-
20	90	5.82	3.16	486	201	352	13.0	4.55	*	4.58
21	99	8.07	7.39	444	111	439	-	7.46	4.82	4.69
22	100	8.02	6.92	438	114	434	17.0	6.62	3.77	3.93
23	99	7.97	4.81	447	112	447	-	7.67	5.29	6.02
24	106	7.92	3.86	391	111	279	-	6.53	4.69	4.49
25	109	7.75	7.66	300	120	343	-	6.02	4.07	4.04
26	108	7.90	6.53	466	125	459	-	6.74	3.04	3.62
27	110	7.84	7.09	284	118	340	-	6.40	4.23	3.88
28	84	6.58	1.78	426	110	424	-	4.49	*	4.34
29	104	7.95	7.44	276	104	328	-	4.76	3.86	-
30	99	8.04	7.39	436	108	430	-	6.09	3.87	3.74

*Insufficient solids to make determination.

TABLE B-4. CHEMICAL ANALYSIS RESULTS - SCRUBBER BOTTOMS SLURRY

Number	Temp. (F°)	pH	Solids Content (Wt %)	Aqueous Phase Concentration (mmol/ℓ) Mg^{+2}	Aqueous Phase Concentration (mmol/ℓ) SO_3^{-2}	Aqueous Phase Concentration (mmol/ℓ) Total Sulfur	Aqueous Phase Concentration (mmol/ℓ) Cl^-	Solid Phase Concentration (mmol/g) Mg^{+2}	Solid Phase Concentration (mmol/g) SO_3^{-2}	Solid Phase Concentration (mmol/g) Total Sulfur
1	108	5.82	4.26	477	386	414	-	4.40	4.55	4.65
2	100	5.65	2.99	884	266	410	-	4.74	4.35	4.51
3	108	5.98	1.84	467	241	426	-	4.63	4.21	4.49
4	102	5.64	2.15	564	295	524	-	4.54	4.41	4.64
5	108	6.22	5.98	474	228	461	-	4.69	4.82	5.32
6	108	5.90	2.15	-	271	429	11.1	4.74	4.63	4.60
7	109	5.54	36.20†	531	443	441	-	4.76	3.68	4.51
8	113	6.04	2.08	506	283	455	13.1	4.74	4.36	4.46
9	115	6.40	3.33	496	233	401	-	4.87	4.37	4.39
10	108	5.84	6.88	501	387	478	14.5	4.50	4.41	4.57
11	109	5.58	8.23	558	405	482	13.5	4.71	4.58	4.68
12	109	5.53	1.76	540	392	422	-	4.41	4.32	4.47
13	99	4.88	0.25	698	543	668	-	4.87	*	4.33
14	102	5.39	1.80	443	402	348	-	5.35	4.48	4.46
15	102	5.74	2.09	539	367	434	-	8.15	6.56	6.93
16	109	4.85	0.20	632	544	542	-	*	3.74	4.83
17	104	5.07	1.66	659	573	613	16.9	5.62	5.13	5.21
18	109	5.37	1.20	575	414	461	-	4.73	4.59	4.61
19	106	4.63	0.07	476	569	674	-	*	*	*
20	97	4.39	0.11	538	375	588	13.0	*	*	*
21	100	5.12	2.14	687	544	674	-	7.16	6.69	7.10
22	95	5.47	4.47	608	397	684	17.0	4.80	4.62	-
23	84	5.74	5.19	557	277	577	-	4.75	4.55	4.86
24	102	5.67	7.10	558	355	378	-	6.45	5.68	-
25	111	5.68	3.54	474	354	520	-	4.89	4.53	4.45
26	109	6.80	8.41	514	165	495	-	5.08	3.95	4.38
27	106	5.07	1.21	551	603	663	-	4.80	4.47	4.49
28	97	5.28	0.22	479	232	441	-	*	*	4.05
29	109	4.96	0.29	591	523	587	-	*	*	*
30	100	4.79	0.46	739	626	547	-	4.64	4.03	4.55

*Insufficient solids to make determination.
†Not a representative sample. Extra solids from downcomer were sucked up.

APPENDIX C

DEVELOPMENT OF THE DESIGN EQUATION

The fractional removal efficiency R (equation 4-9, page 42) is defined as:

$$R = \frac{\gamma in - \gamma out}{\gamma in} \tag{C-1}$$

$$R = 1 - \frac{\gamma out}{\gamma in} \tag{C-2}$$

where γ represents the concentration of SO_2 in the respective streams entering (γin) and exiting (γout) the absorber. From equation 4-8, page 42, we have:

$$\ell n \left(\frac{\gamma in}{\gamma out}\right) = \frac{K_g aPV}{G} \tag{C-3}$$

or

$$\frac{\gamma out}{\gamma in} = \exp\left(-K_g aPV/G\right) \tag{C-4}$$

Substituting the concentration ratio from equation (C-4) into equation (C-2), the following expression is obtained.

$$R = 1 - \exp\left(-K_g aPV/G\right) \tag{C-5}$$

For the packed scrubber used in these tests, the bed volume is:

$$v = D \cdot A_c \tag{C-6}$$

and

$$R = 1 - \exp\left(-K_g aP \cdot D\, A_c / G\right) \quad \text{(C-7)}$$

then

$$1-R = \exp\left(-K_g aP \cdot D\, A_c / G\right) \quad \text{(C-8)}$$

and

$$-\ln(1-R) = K_g a \cdot P \cdot D \cdot \frac{A_c}{G} \quad \text{(C-9)}$$

K_g - is the overall mass transfer coefficient
a - is the amount of interfacial mass transfer area
P - is the total pressure
v - is the scrubber volume (of packing)
D - is the depth of packing
A_c - is the cross sectional area of the absorber
G - is the molar gas flow rate.

Because a precise expression for $K_g a$ cannot be derived from theory, it must be empirically derived. This is accomplished through a linear regression analysis of the empirical data obtained in the test runs as follows:

$$K_g a = b_0 \cdot \left(\frac{L}{A_c}\right)^{b_1} \cdot (SO_2)^{b_2} \cdot (pH)^{b_3} \cdot (W)^{b_4} \cdot \left(\frac{G}{A_c}\right)^{b_5} \quad \text{(C-10)}$$

This expression is substituted into equation (C-9) to give:

$$-\ln(1-R) = \left[b_0 \cdot \left(\frac{L}{A_c}\right)^{b_1} \cdot (SO_2)^{b_2} \cdot (pH)^{b_3} \cdot (W)^{b_4} \cdot \left(\frac{G}{A_c}\right)^{b_5} \right] \cdot P \cdot D \cdot \frac{A_c}{G} \quad \text{(C-11)}$$

and, taking the natural log, simplifying, and rearranging

$$\ln(-\ln(1-R)) - \ln(D) = \ln b_0 + b_1 \ln(L) + b_2 \ln(SO_2) + b_3 \ln(pH)$$

$$+ b_4 \ln(W) + (b_5 - 1) \ln(G) \quad \text{(C-12)}$$

Because the total pressure equals 1 atmosphere, the P term is dropped. Since the area term A_c is a constant, it will affect only the b_0 coefficient.

TABLE C-1. TEST DATA SUMMARY (English Units)

Test Number	R Fractional Removal Efficiency	D Bed Depth (inches)	L Liquor Rate (gpm)	SO_2 Inlet Concentration (ppm)	pH	W Weight % Slurry Solids (%)	G Inlet Gas Flow Rate (scfm)
1	.44	20	7.8	8674	7.81	7.76	1678
2	.57	20	15.7	7414	7.70	4.97	1770
3	.68	20	24.4	7457	7.77	3.17	1769
4	.43	20	9.1	8200	8.03	4.04	2102
5	.65	20	19.0	8093	7.82	6.60	2093
6	.71	20	30.3	8200	7.76	3.43	2106
7	.49	20	10.2	8047	7.74	3.81	2431
8	.66	20	23.0	8309	7.85	3.70	2434
9	.76	20	30.6	7837	7.83	3.66	2430
10	.73	50	6.2	8756	7.99	10.40	1773
11	.88	50	14.8	8123	7.77	4.40	1772
12	.96	50	22.1	7822	7.71	5.22	1771
13	.77	50	7.9	6234	8.03	4.75	2094
14	.95	50	13.3	7616	7.99	7.92	2108
15							
16	.79	50	9.4	7986	7.76	6.22	2491
17	.95	50	16.9	8466	7.73	10.3	2420
18	.97	50	21.0	8078	7.74	4.97	2431
19	.55	50	9.4	8594	6.63	5.56	2433
20	.44	50	9.4	6883	5.82	3.16	2429
21	.92	50	9.4	6030	8.07	7.39	2434
22	.95	50	9.4	4605	8.02	6.92	2434
23	.96	50	9.4	2354	7.97	4.81	2434
24	.98	50	26.9	8093	7.92	3.86	2626
25	.54	20	14.3	8674	7.75	7.66	2439
26	.94	20	38.5	7748	7.90	6.53	2434
27	.91	50	13.8	9260	7.84	7.09	2435
28	.54	20	24.4	9885	6.58	1.78	1764
29	.78	50	9.4	9190	7.95	7.44	2433
30	.81	50	9.4	8200	8.04	7.39	2434

It is omitted from the regression equation and is incorporated later into the b_0 term.

The data given in Table C-1 were used in a regression analysis. On the first trial, the b_5 coefficient is essentially 1, and therefore the G term drops out as insignificant. The regression analysis is then performed a second time for the remaining terms with the following results: b_0 = 0.00187, b_1 = 0.8986, b_2 = -0.6214, b_3 = 2.8641, and b_4 = 0.2837. The liquid rate L is in gallons per minute; it must be adjusted to liters per second for use in the metric SI system, normalized for the cross-sectional area term, and adjusted for the bed depth conversion from inches to centimeters.

$$b_0(\text{adjusted}) = b_0 \left(\frac{60 \text{ sec/min}}{3.785 \text{ ℓ/gal}} \right)^{0.8986} (0.453 \text{ m}^2)^{0.8986} \frac{1 \text{ m}}{2.54 \text{ cm}}$$

$$b_0 = 4.35 \times 10^{-3}$$

As part of its quality assurance program, the IERL-Cincinnati performed the regression analysis independently. The test data was converted to metric units (Table C-2) and then the first regression of equation C-12 was performed. The results confimed the insignificance of the G term. This term was dropped and the regression again performed with the remaining terms. The results, given below, show very good agreement.

Term	Coefficient	Value	
		IERL	Radian
Constant	b_0	0.00438	0.00435
L	b_1	0.89906	0.8986
SO_2	b_2	-0.62234	-0.6214
pH	b_3	2.86343	2.8641
W	b_4	0.28317	0.2837

The b_0 constant is determined from the intercept term given in Table C-4 as follows

TABLE C-2. TEST DATA SUMMARY

Test Number	R Fractional Removal Efficiency	D Bed Depth (cm)	L Liquor Rate (ℓps)	SO_2 Inlet Concentration (ppm)	pH	W Weight % Slurry Solids (%)	G Inlet Gas Flow Rate (Nm^3/hr)
1	0.44	50.8	0.492	8674	7.81	7.76	2851
2	0.57	50.8	0.990	7414	7.70	4.97	3008
3	0.68	50.8	1.539	7457	7.77	3.17	3006
4	0.43	50.8	0.574	8200	8.03	4.04	3572
5	0.65	50.8	1.199	8093	7.82	6.60	3556
6	0.71	50.8	1.911	8200	7.76	3.43	3579
7	0.49	50.8	0.643	8047	7.74	3.81	4131
8	0.66	50.8	1.451	8309	7.85	3.70	4136
9	0.76	50.8	1.930	7837	7.83	3.66	4129
10	0.73	127	0.391	8756	7.99	10.40	3013
11	0.88	127	0.934	8123	7.77	4.4	3011
12	0.96	127	1.394	7822	7.71	5.22	3009
13	0.77	127	0.498	6234	8.03	4.75	3558
14	0.95	127	0.839	7616	7.99	7.92	3528
15	0.98	127	1.135	8514	7.87	4.99	3556
16	0.79	127	0.593	7986	7.76	6.22	4233
17	0.95	127	1.066	8466	7.73	10.3	4112
18	0.97	127	1.325	8078	7.74	4.97	4131
19	0.55	127	0.593	8594	6.63	5.56	4134
20	0.44	127	0.593	6883	5.82	3.16	4127
21	0.92	127	0.593	6030	8.07	7.39	4136
22	0.95	127	0.593	4605	8.02	6.92	4136
23	0.96	127	0.593	2354	7.97	4.81	4136
24	0.98	127	1.697	8093	7.92	3.86	4462
25	0.54	50.8	0.902	8674	7.75	7.66	4144
26	0.94	50.8	2.429	7748	7.90	6.53	4136
27	0.91	127	0.871	9260	7.84	7.09	4138
28	0.54	50.8	1.539	9885	6.58	1.78	2997
29	0.78	127	0.593	9190	7.95	7.44	4134
30	0.81	127	0.593	8200	8.04	7.39	4136

$$-4.08078 = \ln b_0$$

$$b_0' = 0.008933$$

normalizing for the area term

$$b_0 = b_0' \times A_c = (0.008933) \times (0.453)^{0.899}$$

$$= 0.00438 .$$

TABLE C-3
Processed Input Data for Regression Analysis

Test Number	Term 1 $\ln(-\ln(1-R))$ $-\ln D$	Term 2 $\ln L$	Term 3 $\ln SO_2$	Term 4 $\ln pH$	Term 5 $\ln W$	Term 6 $\ln G$
1	-4.4729	-0.7093	9.0681	2.0554	2.0490	7.9554
2	-4.0975	-0.0101	8.9111	2.0412	1.6034	8.0090
3	-3.7974	0.4311	8.9169	2.0503	1.1537	8.0084
4	-4.5039	-0.5551	9.0119	2.0832	1.3962	8.1809
5	-3.8793	0.1815	8.9988	2.0567	1.8871	8.1764
6	-3.7145	0.6476	9.0119	2.0490	1.2326	8.1828
7	-4.3234	-0.4416	8.9931	2.0464	1.3376	8.3263
8	-3.8520	0.3723	9.0251	2.0605	1.3083	8.3275
9	-3.5722	0.6575	8.9666	2.0580	1.2975	8.3258
10	-4.5747	-0.9390	9.0775	2.0782	2.3418	8.0107
11	-4.0926	-0.0683	9.0025	2.0503	1.4816	8.0100
12	-3.6752	0.3322	8.9647	2.0425	1.6525	8.0094
13	-4.4591	-0.6972	8.7378	2.0832	1.5560	8.1770
14	-3.7470	-0.1755	8.9380	2.0782	2.0694	8.1837
16	-4.3991	-0.5226	8.9854	2.0490	1.8901	8.3507
17	-3.7470	0.0639	9.0438	2.0451	2.3321	8.3217
18	-3.5896	0.2814	8.9969	2.0464	1.6034	8.3263
19	-5.0692	-0.5226	9.0588	1.8916	1.7156	8.3270
20	-5.3892	-0.5226	8.8368	1.7613	1.1506	8.3253
21	-3.9177	-0.5226	8.7045	2.0882	2.0001	8.3275
22	-3.7470	-0.5226	8.4349	2.0819	1.9344	8.3277
23	-3.6752	-0.5226	7.7639	2.0757	1.5707	8.3275
24	-3.4801	0.5289	8.9988	2.0694	1.3507	8.4034
25	-4.1808	-0.1031	9.0681	2.0477	2.0360	8.3294
26	-2.8935	0.8875	8.9552	2.0669	1.8764	8.3275
27	-3.9654	-0.1381	9.1335	2.0592	1.9587	8.3280
28	-4.1808	0.4311	9.1988	1.8840	0.5766	8.0054
29	-4.4293	-0.5226	9.1259	2.0732	2.0069	8.3270
30	-4.3369	-0.5226	9.0119	2.0844	2.0001	8.3275

TABLE C-4

Regression Analysis Results

First fit including G term

OLS FIT FOR UNCORRECTED DATA

DETERMINANT=0.48042

SUM OF VARIANCE INFLATION FACTORS= 7.288

VARIANCE INFLATION FACTORS: 1.528 1.238 1.502 1.912 1.117

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	BETA COEFFICIENT	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
2	-0.11045	0.49738	0.71540	0.89248	0.90012	0.06633	13.57039
3	8.92901	0.28740	-0.17821	-0.33312	-0.62493	0.11100	-5.63008
4	2.03890	0.07143	0.58748	0.40888	2.85714	0.45781	8.24369
5	1.68790	0.40088	0.02884	0.22785	0.28525	0.08201	3.10010
6	8.22838	0.14221	0.10484	-0.00498	-0.01755	0.18028	-0.08654
DEPENDENT							
1	-4.06078	0.50183					

CORRECTED INTERCEPT -4.54103

R SQUARED 0.83498

F-VALUE 88.12817

STD. ERROR OF ESTIMATE 0.14115

Second fit without the G term

OLS FIT FOR UNCORRECTED DATA

DETERMINANT=0.51436

SUM OF VARIANCE INFLATION FACTORS= 5.884

VARIANCE INFLATION FACTORS: 1.478 1.152 1.468 1.787

VARIABLE NO.	MEAN	STANDARD DEVIATION	CORRELATION X VS Y	BETA COEFFICIENT	REGRESSION COEFFICIENT	STD. ERROR OF REG.COEF.	COMPUTED T VALUE
2	-0.11045	0.49738	0.71540	0.88141	0.88908	0.06387	14.07704
3	8.92801	0.28740	-0.17821	-0.33174	-0.62234	0.10485	-5.83543
4	2.03890	0.07143	0.58748	0.40778	2.88343	0.44283	8.46815
5	1.88790	0.40088	0.02884	0.22828	0.28317	0.08709	3.25127
DEPENDENT							
1	-4.06078	0.50183					

CORRECTED INTERCEPT -4.71798

R SQUARED 0.83494

F-VALUE 88.22025

STD. ERROR OF ESTIMATE 0.13820

TABLE C-5

Statistics on Original Data

INDEPENDENT VARIABLE NO	EIGENVALUE
2	0.3041
3	0.9342
4	1.0704
5	1.6913

COEFFICIENT MULTICOLLINEARITY INDEX = 1.21908
PREDICTIVE MULTICOLLINEARITY INDEX = 1.78955

****

EIGENVALUES

MINIMUM EIGENVALUE	MULTICOLLINEARITY
GREATER THAN 0.3	LOW
BETWEEN 0.1 AND 0.3	MODERATE
LESS THAN 0.1	HIGH

****

MULTICOLLINEARITY INDEX	MULTICOLLINEARITY
COEFFICIENT:	
GREATER THAN 1.6	HIGH
BETWEEN 1.2 AND 1.6	MODERATE
LESS THAN 1.2	LOW
PREDICTIVE:	
GREATER THAN 2.0	HIGH
BETWEEN 1.4 AND 2.0	MODERATE
LESS THAT 1.4	LOW

****

TABLE C-6

TABLE OF RESIDUALS

CASE NO.	Y VALUE	Y ESTIMATE	RESIDUAL
1	-4.47290	-4.53344	0.06054
2	-4.09750	-3.97395	-0.12355
3	-3.79740	-3.68218	-0.11522
4	-4.50390	-4.46508	-0.03882
5	-3.87930	-3.73155	-0.14775
6	-3.71450	-3.52804	-0.18646
7	-4.32340	-4.47330	0.14990
8	-3.85200	-3.72940	-0.12260
9	-3.57220	-3.44679	-0.12541
10	-4.57470	-4.59761	0.02291
11	-4.09260	-4.09159	-0.00101
12	-3.67520	-3.68194	0.00674
13	-4.45910	-4.37700	-0.08210
14	-3.74700	-3.90149	0.15449
15	-4.39910	-4.37744	-0.02166
16	-3.74700	-3.77250	0.02550
17	-3.58960	-3.75038	0.16078
18	-5.06920	-4.92324	-0.14596
19	-5.38920	-5.31817	-0.07103
20	-3.91770	-4.05923	0.14153
21	-3.74700	-3.92809	0.18109
22	-3.67520	-3.63124	-0.04396
23	-3.48010	-3.53475	0.05465
24	-4.18080	-4.01416	-0.16664
25	-2.89350	-3.04351	0.15001
26	-3.96540	-4.07529	0.10989
27	-4.18080	-4.49722	0.31642
28	-4.42930	-4.36251	-0.06679
29	-4.33690	-4.26142	-0.07548

FINAL AUTOCORRELATION COEFFICIENT = -0.02008

FINAL DURBIN-WATSON = 2.01975